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PROTEIN STRUCTURE AND WATER ABSORPTION¹

DOROTHY JORDAN LLOYD

*British Leather Manufacturers' Research Association, London, England**Received August 1, 1937*

The capacity shown by all proteins for absorbing water is a familiar fact to all colloid chemists. There are innumerable studies in the literature dealing with the subject. Dry proteins will absorb water from moist air or from water in the fluid state, and protein sols if placed in a dialyzing bag will, under suitable conditions, draw more water into the bag. The protein particles in solution exert an osmotic pressure; if they carry a net positive or negative charge, they cause the establishment of a Donnan equilibrium among the diffusible ions present, which adds an additional factor to the internal osmotic pressure and causes more water to flow into the system.

It is a comparatively simple matter to work out the conditions controlling the reversible intake of water into a protein sol. There is considerable evidence that some of the water is very closely associated with or "bound" to the protein molecule (2), and it has indeed been suggested (11) that this firmly bound water is actually linked to definite positions in the protein molecule by a coördinate link or hydrogen bond, though it may merely be held in a dynamic equilibrium around the charged centers of the protein zwitterion. The rest of the water held in the system is held by the osmotic equilibrium.

The amount of osmotic water present in any system is controlled by the extent to which the system is free to swell. In a structureless system like a sol, osmotic water flows in until it is balanced by the head of pressure in the osmometer. As soon as structure is present, the mechanical hindrance to swelling, due to the structure, begins to have an effect. This begins to show even in systems as apparently homogeneous as gelatin gels.

Figure 1 shows the swelling of a number of gelatin gels set from sols of varying concentration under varying external conditions. It should be noted that these gels have never been dried out. The original concentration at the moment of setting has a striking and consistent influence on swelling under all conditions (3). This has also been shown by Kunitz

¹ Presented at the Fourteenth Colloid Symposium, held at Minneapolis, Minnesota, June 10-12, 1937.

(12), who found that a 10 per cent gelatin gel forms a stable system which maintains equilibrium with water, while more concentrated gels absorb water and less concentrated gels actually expel water when in contact with water.

If gelatin gels set at different concentrations are dried down before

Weight.
% on dry
weight.

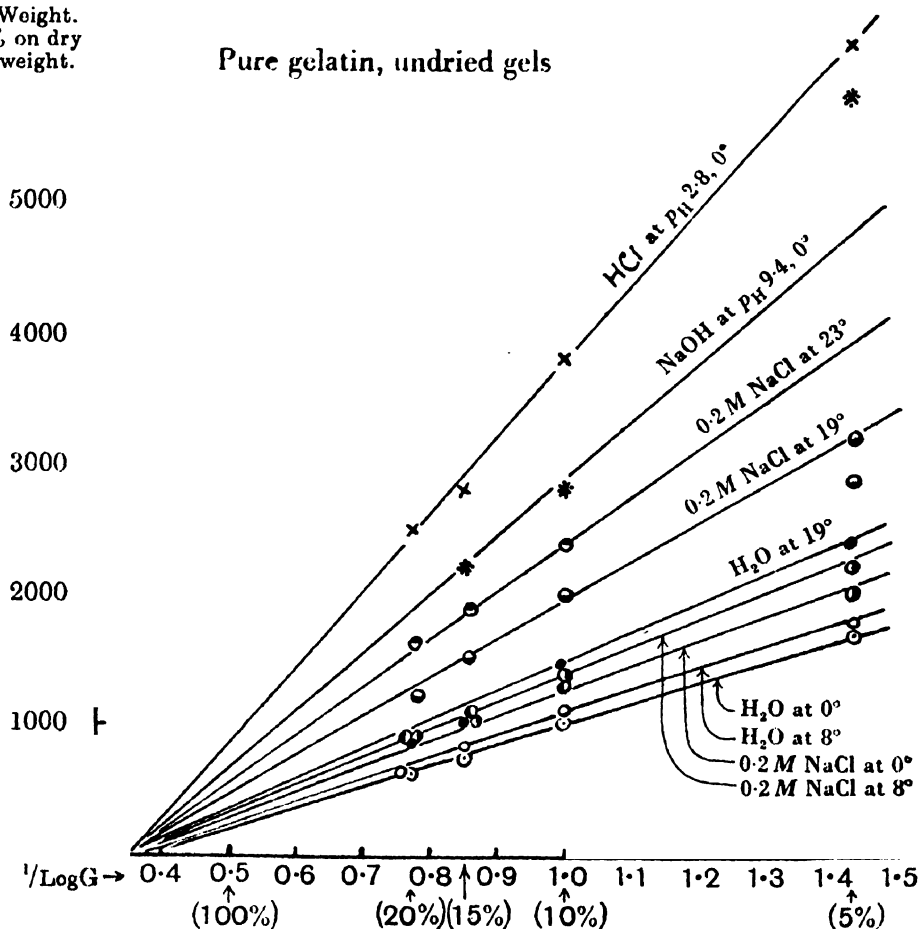


FIG. 1. Swelling of a number of gelatin gels. Ordinate = $1/\log G$, where G = concentration of gel at setting; abscissa = swollen weight of gel as percentage of dry weight.

being placed under the experimental conditions, the effect of the original concentration still persists, and to this is added an additional factor, due to the drying. It is noticeable that gelatin gels once dried never swell to the same extent as before drying.

For gelatin gels which have never been dried out, swelling measured as a percentage gain in weight on the dry weight of the gelatin is a linear

function of $1/\log G$, where G is the percentage concentration of gelatin in the original gel. The simplest inference from this is that the molecules of gelatin in the gel form cross links, making a kind of internal scaffolding throughout the gel, and that the more crowded the molecules, the more rigid the scaffolding. Apparently these molecular cross links are not all

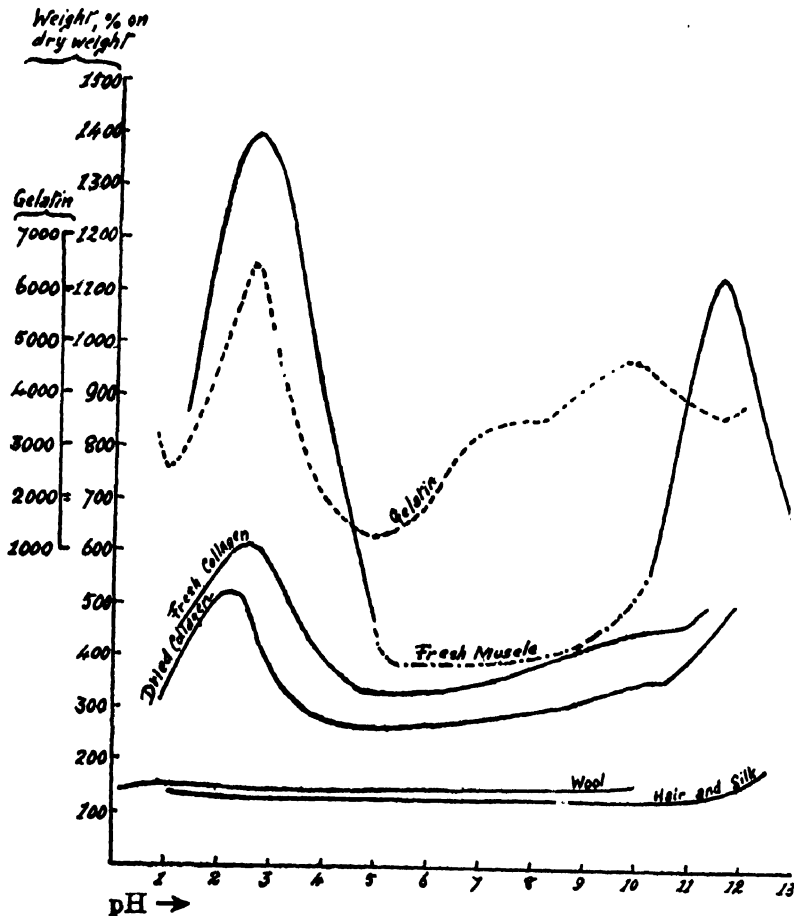


FIG. 2. Comparison of swelling of gelatin with tissues. Note that the gelatin curve is plotted on a reduced ordinate.

readily broken, even by acid or alkali, until fairly high concentrations are reached.

The importance of structure in controlling swelling becomes even more obvious when biological systems are considered. These swell much less freely than gelatin gels, the order of swelling for a tissue containing about 10 per cent of dry matter being about equivalent to that for a gelatin gel containing 30 to 50 per cent of dry gelatin.

Figure 2 shows the swelling in hydrochloric acid and sodium hydroxide of a number of tissues of animal origin, with the swelling of dry leaf gelatin plotted on a reduced scale for comparison (5). There are two noteworthy points shown here:—firstly, that the more water the tissue contains under natural conditions, the greater the degree of swelling under artificial conditions. For instance, frog's muscle contains 80 to 85 per cent water; collagen, in the form of small hide pieces, freed from extraneous proteins, 60 to 65 per cent; and the protein fibers about 12 to 15 per cent. It can be seen in table 1 that the original water content of the tissue, which can

TABLE 1

Percentage of bases and dicarboxylic acids in gelatin and certain tissue proteins, and swelling of gels and tissues expressed as percentage of the swollen weight on the dry weight

Initial concentration of gelatin gel was 12 per cent on setting

PARTS PER 100 PARTS DRY PROTEIN	GELATIN	FROG MUSCLE	COLLAGEN	KERATIN		SILK FIBROIN
				Wool	Horse-hair	
Lysine.....	5.9	7.9	5.9	2.3	1.1	0.2
Histidine.....	0.9	2.5	0.9	0.7		
Arginine.....	8.2	6.5	8.2	7.8	7.6	0.7
Total bases.....	15.0	16.7	15.0	10.8	9	1
Glutamic and aspartic acids...	9.2	19.7	9.2	15.2	4.0	?
Water at minimum swelling...	1200	300 (approx.)	260	40	28	32
Osmotic water at acid maximum.....	5200	1100	230	7	0	0
Osmotic water at alkaline maximum.....	1500	800	120	Osmotic maximum, if any, lost in curve of alkaline solution		

be taken as an inverse measure of the compactness of the structure, is a better indication of the extent of swelling than the number of acid or basic groups which are given by an analysis of the protein. The second point to be noticed is that while gelatin has a well-marked point of minimum swelling under salt-free conditions, the structured proteins show a more or less extended zone of minimum swelling.

The protein fibers, namely, wool, hair, and silk, are held together by a type of internal molecular scaffolding. Salt linkages between amino and carboxyl groups of the side chains of adjacent polypeptide chains and direct linkage between the carbonyl and amino groups of the polypeptide

chains have been suggested (4). Weakening the structure by previous treatment with alkalis leads to an increase of swelling at all reactions. With silk fibers there is a uniform increase of swelling over a wide range of pH values, but hairs, which are characterized by a higher content of dibasic or diacidic residues, show definite maxima in both acid and alkaline regions, after alkaline pretreatment (7, 8).

In considering biological systems, it must not be forgotten that the system may consist of more than one component. Gelatin gels, threads of silk fibroin, and possibly hairs, may be regarded as structures built

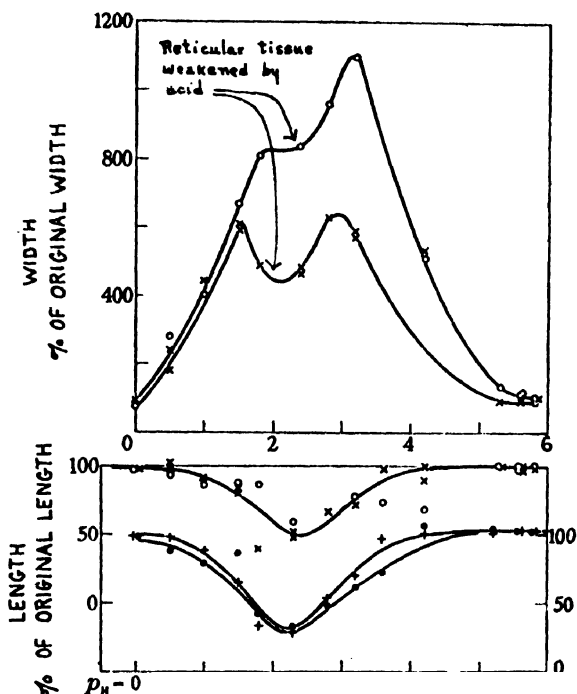


FIG. 3. Swelling of tendons from young (six-weeks old) and old (five-months old) rats in hydrochloric acid solutions. Note that swelling is shown by a contraction in length and an increase in width. \circ and \bullet = old tendons; \times and $+$ = young tendons.

up of a single protein, and held together by internal linkages. Other systems may be more complicated. Collagen fibers, for instance, never consist simply of bundles of collagen molecules in parallel alignment, but have, in addition, a fine investing tissue of reticulin which forms a sheath around the fibers and fiber bundles, possibly even around the fine fibrils. The reticular network investing the fibers is to a certain degree extensible, but tears under sufficient mechanical strain. It is weakened by the action of acid at about normal concentration. The full allowance of reticular tissue seems to be laid down at an early stage of an animal's growth, so

that in half-grown animals the proportion of reticulin to collagen is higher than in fully grown animals (14). Figure 3 shows the swelling at varying pH values in the acid range of tendons from the tails of half-grown and fully grown rats (9). Both curves show a point of maximum swelling near pH 3, and the point at which the acid weakens the reticular tissue is indicated in the figure. The curve for the young tendons is especially interesting, and might lead to some strange calculations did not a microscopical examination reveal the true reason for its shape. In the more dilute acid solutions, swelling is restrained by the reticular tissue; in the more concentrated, the latter is weakened and gives way. Hence, in dilute acids, adult tendons swell more than young; in more concentrated acids, both swell to the same extent. This is illustrated in figure 4.

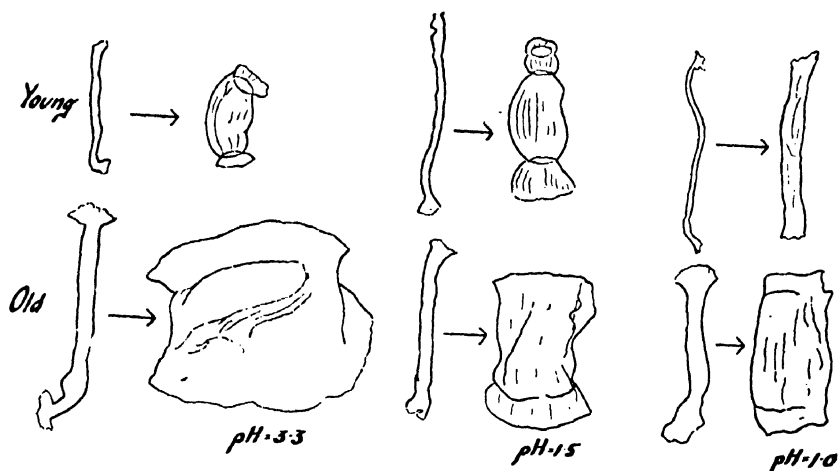


FIG. 4. Swelling of tendons of young (six-weeks old) and old (five-months old) rats in hydrochloric acid solutions. Note complete rupture of reticular tissue in old tendons at pH 3.3.

Another important influence which structure has is on the geometry of swelling. Freshly set gelatin gels appear to swell equally in all directions; dried gels which have been dried under strain, as in the usual method of drying leaf gelatin on nets, expand in all three dimensions, but more freely along the axis where there has been no strain. With the appearance of histological structure, expansion no longer takes place in three dimensions. Silk fibers and hairs expand in diameter only, the length remaining constant, except in a few special circumstances, where marked contraction, or, in the case of hairs, elongation may occur. Collagen fibers swelling in water or salt solutions increase in diameter but not in length, and the increase in diameter occurs evenly all up the fiber. Collagen fibers swelling in acid or alkali shorten in length and increase unevenly in width,

showing bulges and constrictions, where the reticular sheath has or has not given way under the internal osmotic pressure. Figure 4 shows the swellings and constrictions fairly well. Osmotic swelling can be prevented by loading the fiber. If swelling has already taken place, the original length can be restored and the absorbed water can be largely, though never completely, driven out by loading the fiber (10). Under these conditions, however, even a load sufficient to break the fiber does not bring back the original width. Since swelling has been achieved by tearing the reticular sheaths, loading the fiber will obviously not restore these to their places.

The swelling of structured tissue is therefore of two types: the first is due to the drawing in of water by osmotic or other forces against the restraining forces of structure; the second is due to a weakening of the structure, allowing water to pass in simply from its own diffusion pressure. These two types are easy to recognize in practice: the former leads with collagen fibers to a shortening of the swollen fiber, a turgid condition, and a glassy appearance; the latter leads to an increase in diameter only, a flaccid condition, and an opaque appearance, due to the separation of the fibrils in the fiber from each other.

It is not proposed in this paper to enter into a full discussion of the theory of swelling, only to point out that structural features must always be taken into consideration, and that the order of size of the structures concerned may vary from a cross link between one protein molecule and another to the appearance of a second tissue formed from a different protein with characteristic properties.

Imbibition or swelling in water appears to be due to the binding of water at certain localities in the molecule, and in closely packed structures the centers of hydration in two molecules may be linked to each other with the reduction of the amount of water which can be held in this way.

The action of salts, which always promote swelling in the isoelectric region, is probably a solvent action and due to the influence of the salt ions on the multipolar molecule of the proteins leading to a rearrangement of the interionic forces of the system. Salts will not weaken a direct carbonyl-imino linkage between the backbones of adjacent molecules.

Acids and alkalis form salt linkages with the protein zwitterion and lead to the setting up of a Donnan equilibrium. Where the structure is very closely packed, salt formation does not start until a certain potential of hydrogen or hydroxyl ions is reached (1, 6, 15). Thus, in structured systems, minimum swelling occurs over a more or less extended zone. At higher concentrations acids and more especially alkalis weaken protein structures. Possibly the outstanding and universal effect of moderately concentrated strong alkalis in promoting swelling under all conditions lies in the fact that they can break all types of links between protein

molecules, namely, a salt linkage, a carbonyl-imino linkage, and even a disulfide bridge.

With structured tissues such as collagen fibers, the action of sodium hydroxide in promoting swelling through the weakening of the structure can be readily demonstrated. Figure 5 shows the swelling curves of the tendons from rats' tails over a pH range of 9 to 14. In the young tendons

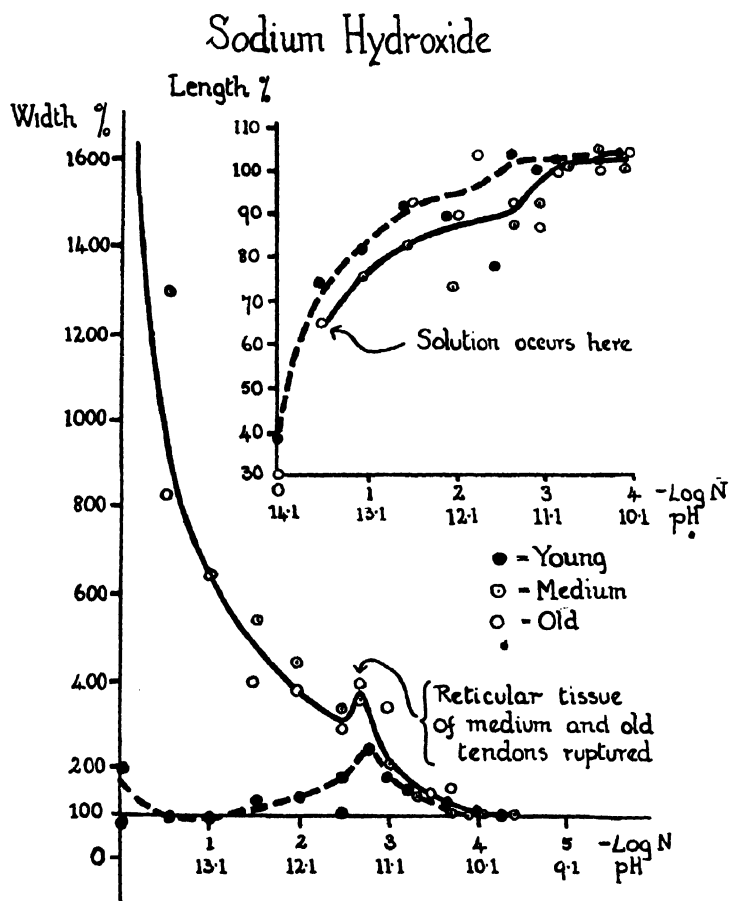


FIG. 5. Swelling of tendons from young (six-weeks old), medium (three-months old), and old (five-months old) rats in sodium hydroxide solutions. Note that swelling is shown by a contraction in length and an increase in width.

(six-weeks old rats) the reticular tissue is sufficiently strong to resist the tearing forces due to the internal osmotic pressures set up in the sodium hydroxide solutions. The swelling curve of these tendons for varying pH values therefore shows a typical point of maximum swelling such as must occur if swelling is due to a Donnan equilibrium. With the tendons from the "medium" (three-months old) rats, which have practically at-

tained adult dimensions, and also with those from the "old" (five-months old) rats, which are fully grown, the story is somewhat different. The reticular sheaths of these full-sized tendons are not so strong as those of the small ones, and near the point of maximum swelling the reticular tissue gives way, partly as a direct consequence of the internal osmotic pressure and partly because it itself is progressively weakened as a result

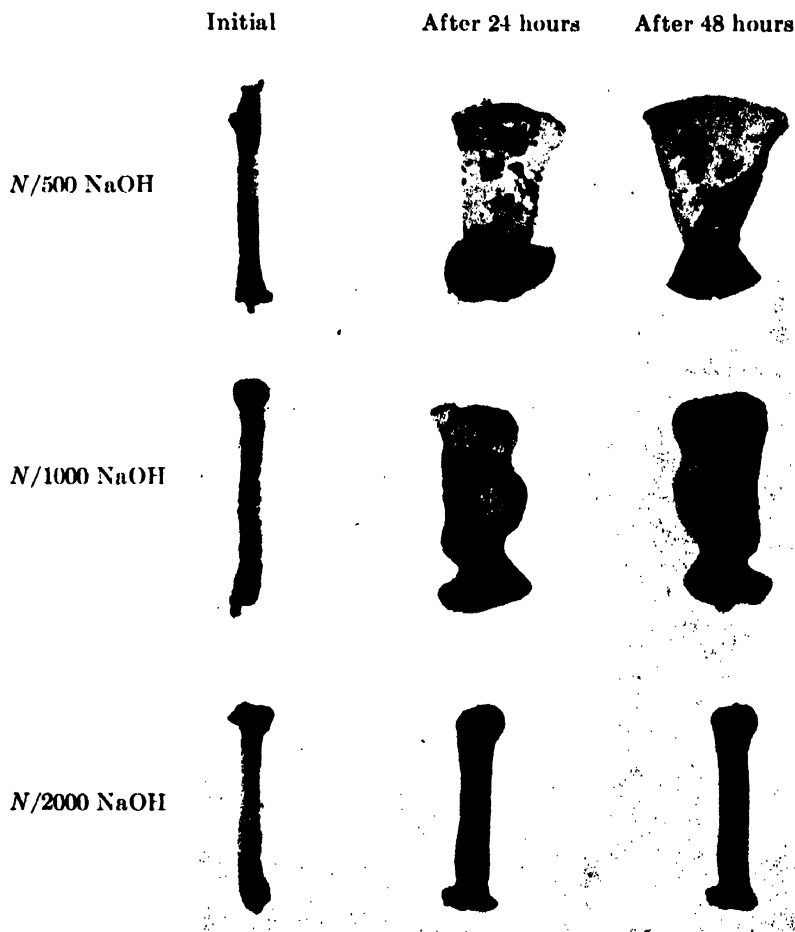


FIG. 6. Swelling of tendons of medium (three-months old) rats in sodium hydroxide solutions. Note mechanical rupture at *N/1000* and progressive weakening at *N/500*.

of the action of the alkali. This is illustrated in figure 6, which shows the behavior of the tendons from the "medium" or three-months old rats. It can be seen that in *N/2000* sodium hydroxide (pH 10.8) there is some swelling, but no rupture of the reticular tissue; moreover, swelling is complete in forty-eight hours. In *N/1000* sodium hydroxide (pH 11.1)

the reticular tissue tears under the internal osmotic pressure, but is not progressively weakened by the alkali, since here again swelling is complete within twenty-four hours. In $N/500$ sodium hydroxide (pH 11.4) the reticular tissue itself is weakened by the action of the alkali. This can be seen by comparing the condition of the tendon after twenty-four and forty-eight hours, respectively. In sodium hydroxide solutions of pH > 11.4 , swelling is progressive with time and leads ultimately to solution.

SUMMARY

The effect of structure on the water absorption of proteins is shown even in such apparently simple systems as gelatin gels. The extent of swelling of these under all conditions is a function of the original concentration at the moment of setting.

The relation between swelling and concentration in freshly made gels can be expressed as $S = f 1/\log G$ where S equals the swollen weight and G the concentration of the gelatin. Gels which have been dried down also show the effect of the original concentration. Dried gels never swell as freely as fresh gels.

Protein fibers and other tissues show a much lower degree of swelling than gels. They also show an extended range of pH values over which no change in weight occurs for a change of pH. Protein tissues swell under varying conditions in proportion to their original water content.

Protein fibers give evidence that swelling is restrained through the presence of a type of internal scaffolding formed by cross links between adjacent protein molecules. In some tissues there is also a type of external scaffolding,—tendons, for instance, have the parallel bundles of collagen molecules sheathed in a fine investing tissue,—and unless the swelling pressure is sufficient to tear this, little swelling occurs.

On account of their complex structure, tissues give more complicated swelling curves than gels.

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THE STUDY OF COLLOIDAL DIMENSIONS, THERMODYNAMIC ACTIVITY, AND THE MEAN MOLECULAR WEIGHT OF THE MIXED PROTEINS IN BLOOD SERUM¹

ANCEL KEYS

Division of Biochemistry, The Mayo Foundation, Rochester, Minnesota

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Estimates as to the molecular weights of blood serum albumin and globulin by the osmotic method (Adair (1, 2, 3, 4, 15)) and by the ultracentrifuge method (Svedberg) are in reasonably close agreement. Serum albumin has a molecular weight of about 70,000, as compared with about 170,000 for globulin. Other things being equal, these values would indicate that at equal concentrations (in units of mass) albumin would have 2.4 times the osmotic activity of globulin.

In biological systems the proteins occur as mixtures, and the relation between the total colloid osmotic activity and the several components in such mixtures is of importance. This is particularly true of blood serum, in which it is generally believed that the osmotic activity of the colloids (almost entirely proteins) is a primary force involved in the preservation of the fluid balance between blood and tissue. In the literature on this subject there are a number of discrepancies, -disagreements with theoretical requirements as well as in the detailed numerical results.

Previous investigators have sought, empirically, to formulate an equation which will describe the relation between colloid osmotic pressure and the concentration of the proteins in blood serum (cf., e.g., 6, 8, 17). In blood serum the proteins are albumin and globulin (plus an insignificant amount of fibrinogen), and, if we may accept the application of Dalton's law of partial pressures to this system (cf. Adair (1)), the relation must be of the form:

$$\text{Colloid osmotic pressure} = f'A + f''G \quad (1)$$

i.e., the C. O. P. will be the sum of a function of the albumin concentration and a function of the globulin concentration. The simplest form these

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functions could take would be as coefficients, i.e., constants for multiplication:

$$\text{C. O. P.} = k'A + k''G \quad (2)$$

Values for k' and k'' have been obtained for human blood serum by Govaerts (8) and von Farkas (6):

$$\text{C. O. P. (mm. H}_2\text{O)} = 75.4A + 19.5G \text{ (Govaerts)} \quad (3)$$

$$\text{C. O. P. (mm. H}_2\text{O)} = 68A + 25.1G \text{ (von Farkas)} \quad (4)$$

where the concentrations of albumin and globulin are in grams per 100 cc. and the temperature is about 20°C.

Recently, Wells, Youmans, and Miller (17) have proposed the formula:

$$\text{C. O. P.} = \text{Total protein} (21.4 + 5.9A) \quad (5)$$

Curiously enough, these authors stress the point that their formula omits globulin, and they argue that globulin is without any important effect. It would seem, however, that their formula (5) should be written:

$$\text{C. O. P.} = (A + G) (21.4 + 5.9A) \quad (6)$$

or

$$\text{C. O. P.} = 5.9A^2 + 21.4A + 5.9AG + 21.4G \quad (7)$$

The data of Wells and his colleagues may be fitted to equation 2 above by the method of least squares². When this is done we have:

$$\text{C. O. P.} = 71.5A + 8.5G \quad (8)$$

as the best fit for these data.

In this laboratory we have studied the C. O. P., albumin and globulin, in serums from fourteen subjects, with at least two experiments on each; eight of these subjects were normal, while six were patients with cirrhosis of the liver. Colloid osmotic pressure measurements were made in duplicate at 0°C. by the classical equilibration method as applied by Adair. Proteins were estimated by the Kjeldahl method, using the factor 6.25 to convert nitrogen to protein concentration; separation of albumin and

² The least squares equations for the general type equation,

$$\text{C. O. P.} = k'A + k''G$$

are:

$$\Sigma A(\text{C. O. P.}) = k'\Sigma A^2 + k''\Sigma AG \quad (1)$$

$$\Sigma G(\text{C. O. P.}) = k'\Sigma AG + k''\Sigma G^2 \quad (2)$$

globulin was made by the method of Howe (10). These data were fitted to equation 2 (above) by the method of least squares with the result:

$$\text{C. O. P. (mm. H}_2\text{O)} = 45.2A + 18.8G \quad (9)$$

The numerical values for k' and k'' in the equations given above (3, 4, 8, and 9) cannot be compared directly, for reasons which will be discussed below, but the ratios of the osmotic activity in serum of albumin to globulin, k'/k'' , may be compared. This is done in table 1.

The colloid osmotic pressure measured in all these studies, as well as the effective force in the living animal, is the sum of the simple osmotic pressure of the proteins as particles and the Gibbs-Donnan effect which arises from the fact that we have to deal with protein ions. The calculation of k'/k'' from molecular weights would be complicated if it could be shown, first, that the Gibbs-Donnan effect is of greatly different magnitude with albumin than what it is with globulin, and, second, that the Gibbs-

TABLE 1

Ratio of the osmotic activity of albumin as compared with globulin in human blood serum

k'/k''	AUTHORITY
3.9	Govaerts (8)
2.7	von Farkas (6)
8.4	Wells, Youmans, and Miller (17)
2.4	Present results
2.4	Simple theory

Donnan effect is a large part of the total gross colloid osmotic pressure as measured in all these studies. It is easy to show that these factors are not of sufficient magnitude to affect the simple calculation of k'/k'' appreciably.

Van Slyke, Hastings, Hiller, and Sendroy (16) have shown that at pH = 7.35 the base-combining power of albumin is about 1.4 times as great as that of globulin; in other words, the Gibbs-Donnan effect will be greater with albumin than with globulin. In blood serum in the physiological range of pH the Gibbs-Donnan effect is of the order of 20 per cent of the total colloid osmotic pressure when the A/G ratio is about 1.8. Under the same conditions of salt concentration and pH, the Gibbs-Donnan effect would be of the order of 16.5 per cent of the total C. O. P. in a pure globulin solution and slightly less than 22 per cent in a pure albumin solution. Accordingly, the maximum error from the neglect of the difference in Gibbs-Donnan effect in albumin and in globulin solutions would be less than 5.5 per cent. In the living organism, even under pathological conditions, the variation in A/G is restricted, so that

the greatest error that could arise from this source would still be less than 5 per cent of the total colloid osmotic pressure.

The effect of pH must also be considered. The pH of different samples of serum will vary slightly and the conditions of measurement of the C. O. P. may accentuate this variation. Since the isoelectric points of albumin and globulin are nearly the same (cf. Van Slyke and others (16)), there can be no significant differential effect on albumin as opposed to globulin and again it must be concluded that the constancy of the ratio k'/k'' will be almost entirely unaffected. •

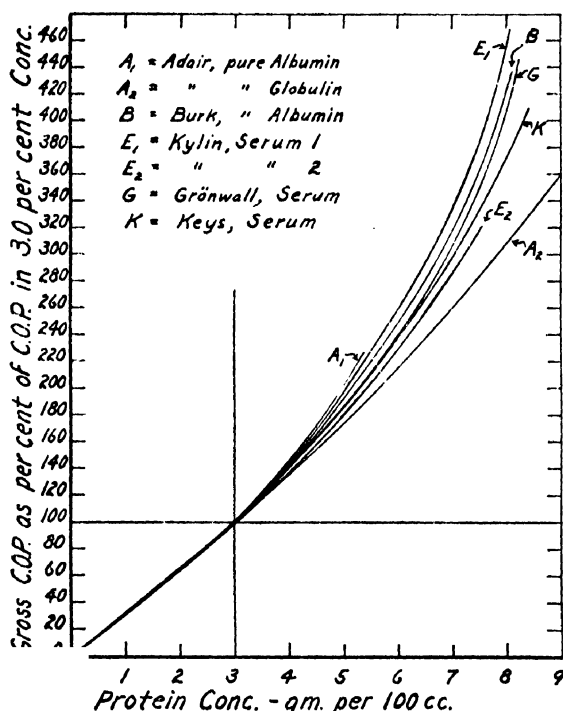


FIG. 1. The effect of protein concentration on the relative gross colloid osmotic pressure. Temperatures in separate series from 0° to 22°C.

Marrack and Hewitt (14) found that variations in pH have a definite effect on the C. O. P., but this is so small that, over the range pH 6.7 to 7.7, even the absolute magnitudes of k' and k'' will change no more than 4 to 8 per cent.

It has long been known that when the concentration of a protein solution is increased the colloid osmotic pressure increases more than in simple linear proportion. In other words, the values of k' and k'' in equation 2 are not independent of the total protein concentration. This in itself is sufficient to account for some of the apparent discrepancies in the osmotic coefficients reported in the literature. The correction for this effect in

blood serum would be relatively simple if it could be shown that the effect of protein concentration on the C. O. P. is not dissimilar in different mixtures of albumin and globulin. Figure 1 shows that this is indeed the fact at protein concentrations below 6 per cent. Even at 8 per cent concentration it is probable that differences in the effect of concentration on the osmotic activity of albumin as compared with globulin are relatively insignificant.

It is clear that equation 2 may now be extended to cover more than a fixed level of total protein concentration:

$$\text{C. O. P.} = f_c(k'A + k''G) \quad (10)$$

For measurements at 0°C., we may use the data of the experiments reported in this paper:

$$\text{Gross C. O. P. (mm. H}_2\text{O)} = f_c(45.2A + 18.8G) \quad (11)$$

Values for f_c for various concentrations of total protein are listed in table 2.

TABLE 2

Values of f_c in the equation: C. O. P. = $f_c(k'A + k''G)$

General relation between f_c and protein taken from averages of data given in figure 1.

Absolute numerical values calculated from results with twenty-eight samples of blood serum with average protein concentrations, including experiments with dilutions, of 3.49 g. per 100 cc.

PROTEIN grams/100 cc.	f_c	PROTEIN grams/100 cc.	f_c	PROTEIN grams/100 cc.	f_c
1.0	0.88	3.5	1.00	6.0	1.17
1.5	0.90	4.0	1.03	6.5	1.22
2.0	0.92	4.5	1.06	7.0	1.28
2.5	0.95	5.0	1.09	7.5	1.35
3.0	0.98	5.5	1.12	8.0	1.45

So far we have attempted to provide a relation between serum albumin and globulin concentration and C. O. P. and have extended this to cover variations in total protein concentration from 1 to 8 g. per 100 cc. The numerical values of the coefficients, however, are based on constant temperature (0°C.), constant pH (7.2 to 7.4), and constant salt concentration. Variations in these factors must now be considered.

The effect on the C. O. P. of variation in the salt concentration is illustrated in figure 2. The pathological extremes in salt concentration are less than ± 10 per cent of the normal salt concentration of the serum; this range corresponds to less than ± 1 per cent of the gross C. O. P. It must be concluded that variations in the salt concentration in all natural serums are too slight to have any appreciable effect.

The extreme range, compatible with life, for the pH of the serum in man is perhaps 6.6 to 7.8, but the range which may be endured for more than an hour or so is probably no greater than from pH 6.9 to 7.6. Differences in pH of this amount will affect the C. O. P. by less than 6 per cent of the total pressure (Marrack and Hewitt (14); cf. above). Obviously the effect of variations in pH may be neglected as a first approximation, unless the pH of the serum is altered experimentally *in vitro*.

The effect of temperature on the colloid osmotic pressure of serum or serum proteins has been little studied. From the simple van't Hoff equation, $p = cRT$, it might be expected that the C. O. P. would vary in

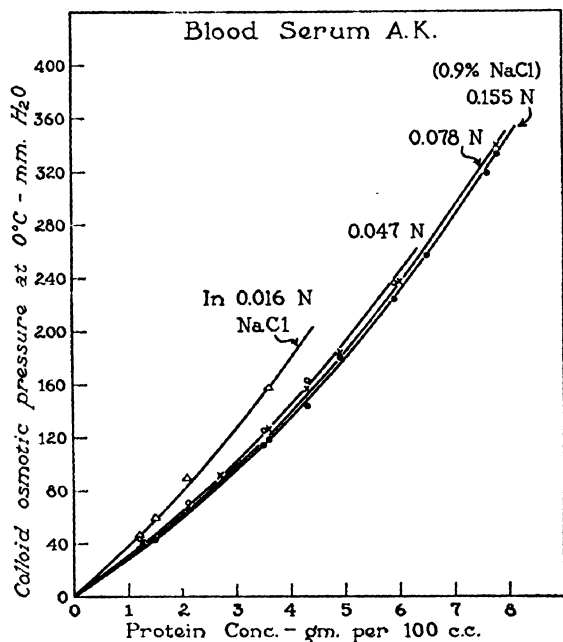


FIG. 2. Relations between gross colloid osmotic pressure, protein concentration, and salt concentration in various dilutions of normal human serum. All values at pH = 7.4 and $T = 0^{\circ}\text{C}$.

direct proportion to the absolute temperature. Some comparisons of the C. O. P. measured in human blood serum by the method of Krogh and Nakazawa (12) at 22°C . and by the method of Keys and Taylor (11) at 0°C . indicate that this is approximately the case for a limited range of temperature, and we may write, tentatively:

$$\text{C. O. P.} = f_c (45.2A + 18.8G) \times \frac{T(^{\circ}\text{Absolute})}{273} \quad (12)$$

So far in this paper the main concern has been to provide a reasonable basis for mathematical description and comparison of measurements of

the gross colloid osmotic pressure in mixtures of albumin and globulin such as blood serum. It must be recognized at the outset that the sharp division of plasma proteins into discrete entities labelled "albumin" and "globulin" is largely a matter of convenience. There is no reason to doubt that there are distinct species of proteins in blood plasma which correspond, at least roughly, to what we refer to as albumin and globulin, but it is much less certain that these protein types are quantitatively separable, with unvarying precision, by any present-day methods. This does not, however, invalidate the use of these terms in a *mathematical* formulation of the relations between the amounts of these types and the osmotic effects of mixtures of them. Such a formulation is a preliminary step toward the practical application of the classical laws of thermodynamics to a complex system such as blood plasma. Some outlines of the further analysis of the system, in terms amenable to experimental attack, may be given here.

Consider the equilibrium of a system when blood plasma or serum is separated from a protein-free transudate by a crystalloid-permeable, colloid-impermeable membrane (such as the capillary membrane in man). The essential variables may be represented, for the physiological range pH 6.5 to 8.0:

I	II
SUBSTANCE	SUBSTANCE
<p>P = Protein P⁻ = Proteinate BP⁺ = Base bound by protein B⁺ = Free base H⁺ Cl⁻ A⁻ = All other anions</p>	<p>Total base = B⁺ H⁺ Cl⁻ All other anions = A⁻</p>

We shall denote the Gibbs chemical potential by $\{ \quad \}$, where $\{ \quad \} = \alpha [\quad]$, where α is an osmotic coefficient and the square brackets denote equivalent concentrations. Subscripts 1 and 2 will be used to distinguish the serum and the transudate phases respectively. As a first approximation we may assume that all ions except proteinate are univalent; this can create no very great error in natural biological systems where, in fact, less than 5 per cent of the free ions are multivalent.

Applying Dalton's law of partial pressures we have (13):

$$\text{C. O. P.} = RT\{[P] + [P^-]\} + RT\{[A^-]_1 + [Cl^-]_1 + [BP^+] + [B^+]_1 - [B^+]_2 - [Cl^-]_2 - [A^-]_2\}^*$$

* Note that H⁺ is omitted; the number of hydrogen ions present is so small as to be negligible in summing up all ions or molecules.

From the application of Gibbs-Donnan equilibria, we have:

$$\frac{[\text{Cl}^-]_1}{[\text{Cl}^-]_2} = \frac{[\text{A}^-]_1}{[\text{A}^-]_2} = \frac{[\text{H}^+]_2}{[\text{H}^+]_1} \quad (14)$$

and also:

$$E = \frac{RT}{F} \ln \frac{1}{\lambda} \quad (15)$$

where E is the membrane potential and λ is the ion ratio (in activities) for the distribution of any diffusible ion between the two phases. In another form we may write the equation for the Gibbs-Donnan equilibrium:

$$[\text{B}^+]_2 \{[\text{Cl}^-]_2 + [\text{A}^-]_2\} = \{[\text{Cl}^-]_1 + [\text{A}^-]_1\} \{[\text{A}^+]_1 + [\text{B}^+]_1\} \quad (16)$$

From the principle of electrical neutrality, we have:

$$[\text{A}^-]_2 = [\text{B}^+]_2 - [\text{Cl}^-]_2 \quad (17)$$

and

$$[\text{BP}^-]_1 = [\text{P}^-]_1 + [\text{A}^-]_1 + [\text{Cl}^-]_1 - [\text{B}^+]_1 \quad (18)$$

Finally, we have, for the true colloid osmotic pressure of the protein alone:

$$(\text{C. O. P.})_0 = \text{C. O. P.}' - RT \{ [\text{BP}^+]_1 + [\text{B}^+]_1 + [\text{Cl}^-]_1 + [\text{A}^-]_1 - [\text{B}^+]_2 - [\text{Cl}^-]_2 - [\text{A}^-]_2 \} \quad (19)$$

and, following van't Hoff:

$$(\text{C. O. P.})_0 = \frac{(\text{Tot. prot.})}{\frac{(\text{Mol. wt.})}{V}} RT \quad (20)$$

where (Tot. prot.) represents the mass of the proteins, and V the solvent volume.

The equations given here are presented as a guide to the further study of natural solutions of proteins. It should be obvious that, in the last equation (20), the separation of total protein into albumin and globulin may be done by the utilization of the arguments and equations (2 through 9) presented in the first part of this paper, and that this need not involve, necessarily, a precise laboratory method for the quantitative separation of the two chief varieties of protein.

For a preliminary application of the arguments given here, the necessary

measurements, in a membrane system separating serum from a protein-free transudate at equilibrium, are: (1) (Tot. prot.); (2) $[Cl^-]_1$ and $[Cl^-]_2$; (3) $[H^+]_1$ and $[H^+]_2$; (4) [Tot. base]₁ and [Tot. base]₂; (5) E (the membrane potential); (6) C. O. P. (the gross colloid osmotic pressure); (7) temperature (T); and (8) V (the solvent volume). Simultaneous measurement of all these variables is technically feasible, and from them, by use of the foregoing equations, it should be possible to arrive at satisfactory values in this complex system for: α_{Cl^-} , $\alpha_{prot.}$, $[BP^+]$, and the mean molecular weight of the mixed proteins. In addition, there are sufficient cross checks so that any gross deviation from theory should be readily apparent.

Preliminary experiments indicate that, in fact, there do not appear to be any important factors not yet considered in the foregoing tentative analysis. Detailed results will be presented at another time.

SUMMARY

Discrepancies in the literature between the molecular weights of serum albumin and serum globulin and their reported osmotic effects in the mixtures occurring in blood serum are principally the result of the limitations of methods for the quantitative estimation of these proteins in the presence of each other. By the use of a variety of precautions an agreement is reached between analytical results and simple theory.

Serum albumin has about 2.4 times the osmotic activity, per gram, exhibited by globulin. It is shown that this relation is not seriously disturbed by variations in pH over the range 6.7 to 7.7, nor by variations in the total protein concentration up to 6 per cent and, with less certainty, up to 8 per cent of the total concentration.

The effect of total protein concentration on the relative colloid osmotic pressure per gram of protein concentration was studied, from which it was concluded that albumin and globulin, and various mixtures of these proteins, exhibit nearly the same effect, quantitatively, up to around 8 per cent concentration. A table of conversion factors is given, as well as numerical constants for the osmotic activities of the two proteins.

Equations are presented which describe the relations of the activity coefficients of the proteins and of chloride in the presence of the proteins, the protein concentration, the molecular weight of the proteins, the membrane potential, and the gross colloid osmotic pressure. The analysis provides a reasonable preliminary guide to the further thermodynamic study of the complex system of blood serum and a transudate.

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OSMOMETRIC STUDY OF GUM ACACIA SOLUTIONS USED FOR INTRAVENOUS INJECTION¹

HUGH R. BUTT AND ANCEL KEYS

Division of Biochemistry, The Mayo Foundation, Rochester, Minnesota

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Intravenous injections of gum acacia solutions are widely used, clinically, to increase the colloid osmotic pressure (C. O. P.) of the blood plasma. In addition to the lack of available data on the effects of such injections on the total C. O. P. of the blood plasma, there is a discrepancy in the reported C. O. P. values, or mean particle size, in simple gum acacia solution itself. This is probably the result of several factors, among which importance may be given to variations in individual samples of gum acacia, especially with regard to particle size and sodium and calcium content.

The basic structure of gum acacia is a galactoso-glucuronic acid (3, 8). Primarily it is a mixture of polymerized anhydrides of galactose and arabinose in varying proportions. In the crude state the calcium, potassium, and magnesium salts of arabic acid predominate. It has been repeatedly demonstrated that the sodium salt of gum acacia gives higher C. O. P. values than the calcium salt (2, 7). Perhaps these two factors alone account for part of the discrepancy in the reported values (table 1). However, a variability in the C. O. P. from 8 to 275 mm. of mercury in a single concentration of gum acacia seems large, even if we assume different particle size and salt concentrations. All of these authors, as far as we are aware, assumed that a protein-tight membrane was also impermeable to gum acacia particles. In no instance is there mention that the membranes used were "acacia-tight" or that the outer medium was tested for the presence of gum acacia.

In this investigation we first attempted to measure the C. O. P. of 6 per cent gum acacia, using tested protein-tight collodion sacs suspended in a suitable medium at 0°C. Regardless of the outer medium (phosphate buffer, physiologic saline solution, or distilled water) the C. O. P. value continued to fall during a period of at least twelve days. Qualitative tests showed that gum acacia entered the outer medium in each instance. When phosphate buffer (pH = 7.4) was the outer medium it was noticed

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that small, grayish-white crystals collected on the outside of the collodion sacs and a few crystals settled out in the bottom of the tube containing the buffer. These were assumed to be, without direct evidence, crystals of calcium phosphate. The membranes employed possessed a permeability to distilled water varying between 0.005 to 0.014 cu. mm. per minute per square centimeter per 1 cm. of water pressure.

The properties of gum acacia sol are greatly changed by the presence of proteins. When 6 per cent gum acacia is added to human blood serum, a stable equilibrium is quickly reached in collodion sac osmometers and there is no evidence of leakage of the acacia through the membrane. There is a rise in the C. O. P. of the serum approximately in proportion to the amount of acacia added (table 2). In the presence of relatively

TABLE 1

Measurements of the colloid osmotic pressure of 6 per cent solutions of acacia

SALT CONTENT OF MEDIUM	pH	COLLOID OSMOTIC PRESSURE	
		mm. Hg.	
0.....		246-275	Pfeffer, 1877
0.....		134	Moore and Roaf, 1907
Na salt.	CO ₂ -free	274	Gasser, Erlanger, and Meek, 1919
Na salt.	CO ₂ -saturated	83	Gasser, Erlanger, and Meek, 1919
0.9 per cent NaCl.....		16	Krogh and Nakazawa, 1927
0.65 per cent NaCl.....		18.6	Drinker, 1927
Locke, slightly modified.	7.3	57.5	Went, 1929
0.....	4.5	56-58	Dodds and Haines, 1934
0.9 per cent NaCl.....	4.2	8.8	Dodds and Haines, 1934
0.9 per cent NaCl.....		11	Onozaki and Sanada, 1935
0.9 per cent NaCl.....	4.292	18	Butt and Keys, 1937

large amounts of protein, the change in C. O. P. attributable to the gum acacia is such as to indicate a mean particle size of the order of 100,000.

Experimentally, Drinker (6) has observed that when a sufficient amount of horse serum is added to an acacia solution, the capillary membrane in contact with the mixture retains its normal semipermeability but does not display the free leakage which appears when acacia alone is used.

Obviously the true C. O. P. of simple gum acacia solutions cannot be obtained by the use of ordinary protein-tight membranes. Membranes of less permeability were prepared by incorporating a water-soluble, non-volatile swelling agent (glycol) in anhydrous ether-alcohol collodion as described by Pierce (14). These membranes had a permeability to distilled water varying from 0.003 to 0.004 cu. mm. per minute per square centimeter per 1 cm. of water pressure. Some of these membranes were

"acacia-tight" and with them equilibration was attained usually within forty-eight hours. The values obtained indicate that a 6 per cent gum acacia solution has a C. O. P. that approximates that of the normal human blood plasma (table 3).

The second phase of the investigation was concerned with the results of intravenous injection of gum acacia solution in humans. Determinations were made of the C. O. P., the serum proteins (albumin and globulin),

TABLE 2

The effect of acacia on the colloid osmotic pressure of normal serum in vitro

DILUTIONS OF HUMAN SERUM WITH BUFFER AND ACACIA	C.O.P. IN MM. OF WATER PER GRAM OF PROTEIN NITROGEN PER 100 CC. OF SERUM	MEMBRANE PERMEABILITY PER CUBIC MILLIMETER PER MINUTE, PER SQUARE CENTIMETER, PER 1 CM. OF WATER PRESSURE
5 cc. of serum 5 cc. of buffer	215	0.005
5 cc. of serum 4.5 cc. of buffer 0.5 cc. of 6 per cent acacia	256	0.003
5 cc. of serum 5 cc. of buffer 0.5 cc. of 6 per cent acacia	255	0.002
5 cc. of serum 4 cc. of buffer 1 cc. of 6 per cent acacia	281	0.011

TABLE 3

Colloid osmotic pressure determinations of gum acacia

SOLUTION	pH	C.O.P. IN MM. OF MERCURY
12 per cent arabic acid.....	7.227	33+
6 per cent arabic acid.....	7.227	13
6 per cent gum acacia (Na salt)...	4.292	18
4 per cent gum acacia (Na salt)...	4.292	5.2

and the fate of the injected acacia in three cases of cirrhosis of the liver and in one of subacute toxic degeneration of the liver.

The gum acacia employed in each case was a 6 per cent (with 0.9*N* sodium chloride) solution sterilized in the autoclave. Mention is made that these solutions were autoclaved, because this process supposedly increases the C. O. P. of the solution (5). Following the intravenous injection of a solution of 6 per cent gum acacia the C. O. P. of the blood

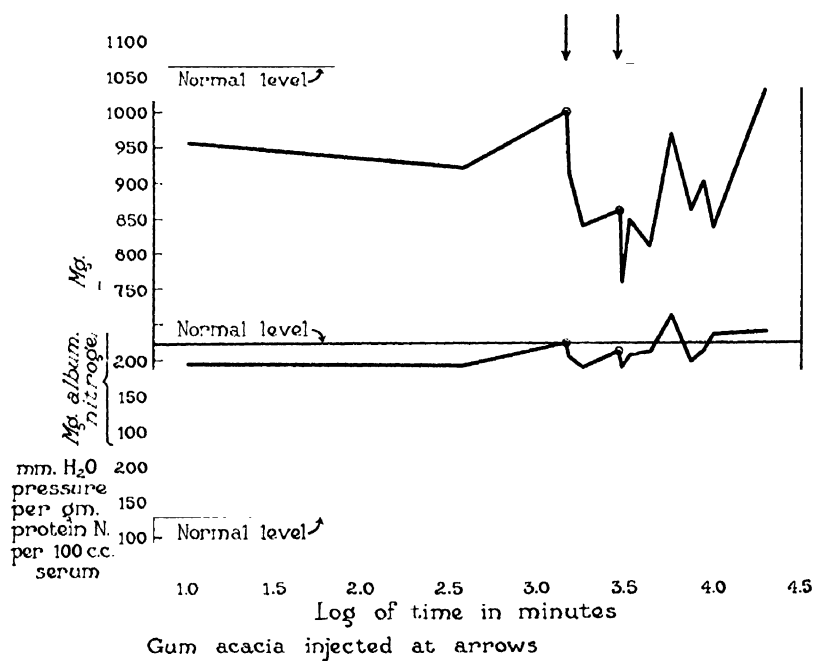


FIG. 1. The effect of the intravenous injection of gum acacia solution in an individual with cirrhosis of the liver.

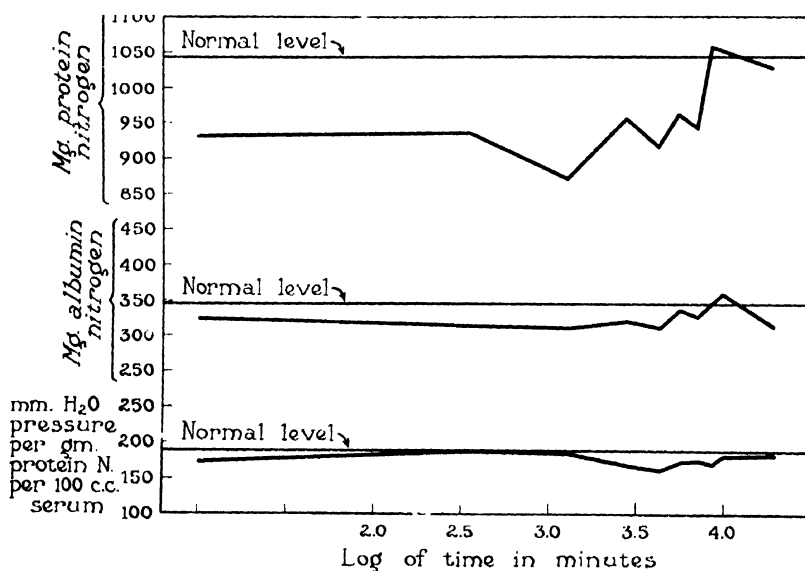


FIG. 2. The effect of injection of 500 cc. of 6 per cent gum acacia in an individual with cirrhosis of the liver.

serum is assumed usually to be elevated only for a period of forty-eight hours (1). However, it will be seen in figure 1 that the C. O. P. of the blood serum remained above the patient's basal level, following the third 500-cc. injection of gum acacia, for a period of four days.

In the case summarized in figure 2 there was only one 500-cc. injection of gum acacia. The C. O. P. of the blood serum in this instance was maintained above or at the basal level for only twenty-four hours.

It is frequently stated in the literature that the serum proteins, particularly the albumin fraction, fall to a low concentration in man and animals following the intravenous injection of gum acacia solution (4). Only

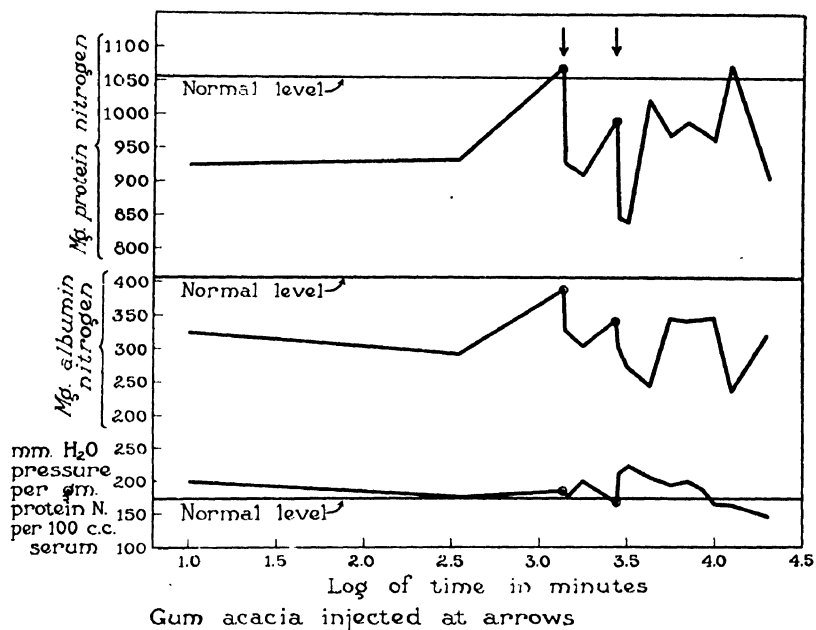


FIG. 3. A case of cirrhosis of the liver showing the occasional reduction of concentration of albumin following the injection of gum acacia solution.

in the case summarized in figure 3 was the albumin concentration decreased appreciably following this procedure, and at no time was this reduction of the magnitude reported in the literature.

DISCUSSION

It seems that the failure to consider the variability of individual gum samples in regard to particle size and salt content, together with the employment of protein-tight rather than acacia-tight membranes, probably accounts for most of the errors in the reported C. O. P. determinations of gum acacia. It is significant that the divergent values reported in the literature are not supported by any acceptable criteria of equilibrium and are in sharp disagreement with the results of cryoscopic measurements.

It appears that the disperse phase in simple gum acacia sols is composed of particles of variable size, with molecular weights ranging perhaps from less than 2000 up to several hundred thousand or more; the observed colloid osmotic pressure of such sols will depend partly on the method of preparation, but more particularly on the permeability of the membrane used.

It is difficult to explain why gum acacia when added to human serum will not leak through a collodion sac from which it previously would escape. Drinker observed increased permeability, dilatation, and edema when a frog's leg was perfused with a buffered 3 per cent gum-saline solution, but these increases disappeared upon the addition of horse serum in amounts greater than 15 per cent to the perfusion medium. His conclusion that serum is necessary for the maintenance of normal capillary tone does not help the understanding of the mechanics of the phenomenon.

In dogs with intact circulations, Stanbury, Warweg, and Amberson (15) have replaced the plasma proteins with gum acacia in saline solution so that the plasma protein level was maintained below 0.2 per cent. These animals were maintained in normal health for months without any symptoms of edema or shock. It appears that some of the functions of the plasma colloids can be replaced, in the experimental animal, by gum acacia solutions sufficiently purified and properly buffered, and in which at least 20 per cent of erythrocytes are suspended. This, however, does not explain why, at the isolated capillary membrane, gum acacia freely leaks through when not mixed with serum. It has been suggested (10) that the value of gum acacia in maintaining blood volume may be the result of its adsorption on the capillary walls, whereby the exit of fluid from the vessel is impeded. However, Amberson and his coworkers have demonstrated that gum acacia alone is not effective in maintaining blood volume if there is an oxygen lack.

SUMMARY

In the concentration usually employed for clinical use (6 per cent), gum acacia behaves as a typical lyophilic colloid that is highly aggregated. It exerts a C. O. P. (18 mm. of mercury) that is nearly equivalent to that of the normal colloids of the plasma.

Gum acacia particles readily leak through ordinary protein-tight membranes but are restrained by membranes of less permeability. The effect of human serum on the permeability of membranes to gum acacia has been discussed.

In four human cases with liver injury the injection of gum acacia was followed by a rise in the C. O. P. of the blood serum with no significant change in the concentration of the albumin or globulin fractions. The C. O. P. of the serum remains markedly elevated for some hours after injections of gum acacia, but this effect disappears in a few days.

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THE INFLUENCE OF GELATIN AND ELECTROLYTE CONCENTRATION ON THE RATIO OF ELECTROÖSMOTIC TO ELECTROPHORETIC MOBILITY¹

H. L. WHITE AND LYMAN FOURT

Departments of Physiology and of Zoology, Washington University, St. Louis, Missouri

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While it has been repeatedly shown that in salt solutions of concentration greater than 1×10^{-2} molar the ratio of electroösmotic to electrophoretic velocity at a gelatin-aqueous interface is unity, White, Monaghan, and Urban (8) presented evidence that this holds true only for electrolyte concentrations above the range 10^{-3} to 10^{-2} molar. At concentrations below this range the ratio of the velocities departs from unity, becoming as high as 2.0. Bull (2) and Moyer and Abramson (7), however, state that with protein surfaces the ratio is unity, even in very dilute salt solutions (conductivities corresponding to 1 to 4×10^{-5} M potassium chloride). The present communication is a partial repetition and an extension of the experiments of White, Monaghan, and Urban and of Moyer and Abramson to investigate the reason for the apparent discrepancy. The present report presents evidence that the observations both of White, Monaghan, and Urban and of Moyer and Abramson are correct, but are not comparable, owing to the influence of the concentration of gelatin employed.

METHODS

A cylindrical Pyrex Mattson-type cell was used. The gelatin was adsorbed on powdered Pyrex particles 1 to 3 micra in diameter. The cell was always allowed to stand at least a half hour, usually an hour or more, filled with the experimental solution, or with this slowly passing through it.

The preparations of gelatin used were as follows: Eastman Purified, ash content 0.03 per cent; Coignet "Silver Lable"; Afga "Lichtfilter" (Ucopoco 6415 "with low ash content"), ash 1.10 per cent. The filtered 1 or 2 per cent stock solutions were kept in the ice box when not in use, and were used within two days or so of preparation.

Observations of the time to traverse a given distance were made and recorded by the same observer. The average was taken of five traverse times in each direction. The mean velocity for a given depth was cal-

¹ Presented at the Fourteenth Colloid Symposium, held at Minneapolis, Minnesota, June 10-12, 1937.

culated from the mean velocities in the two directions. Drift was usually small; in one experiment for which the deviations of the times in each direction were calculated, the deviation was 4.2 per cent.

Readings were taken at a number of levels in the cell, as recommended by Moyer and Abramson. It can be shown that the equation

$$y = b(x - x^2) + c \quad (1)$$

used by them for the flat cell describes the observed velocity at any level in the round cell as well²; y is the observed velocity at any fraction, x , of the diameter from the top; b is the slope of the resulting straight line, and c is the intercept at $x = 0$, i.e., the velocity at the wall. For any given solution, b and c should be constants. Since at the wall $y_0 = c$, c is the difference between the electroösmotic and electrophoretic velocities. In the round cell the ratio is

$$R = \frac{u}{v} = \frac{y_{0.5} - y_{0.147}}{y_{0.147}} = \frac{y_{0.147} - y_0}{y_{0.147}} \quad (2)$$

where the subscripts refer to the fraction of the diameter from the top at which the velocity was observed, and u is the electroösmotic, v the electrophoretic velocity. The values of c , R , u , and v , given in tables 1 and 2 arise not from any single pair of observations but from an application of equation 1 to points obtained throughout the upper half of the cell. In every case the values of $y_{0.5}$, $y_{0.147}$, or y_0 used to determine R according to equation 2 are obtained graphically from the straight-line plots of equation 1, as is illustrated in figures 2 and 3. The values of $y_{0.147}$ and $y_{0.5}$ so obtained agree closely with the values directly observed at these levels. The conclusion that R was unity where there was no observable movement near the wall was confirmed graphically.

² Mattson (J. Phys. Chem. **37**, 223 (1933)) gives the equation

$$V = c \left(r^2 - \frac{a^2}{2} \right)$$

for the velocity, V , of the liquid at any radius, r , from the center in a tube of radius a , c being a constant. The fraction of the diameter measured downwards from the top is

$$x = \frac{a - r}{2a}$$

The observed velocity, y , of a particle is the sum of v , its electrophoretic velocity, and V . In terms of x we have

$$y = V + v = -4ca^2(x - x^2) + \frac{1}{2}ca^2 + v$$

which is of the same form as equation 1 of the text, in which b is $-4ca^2$ and c is $\frac{1}{2}ca^2 + v$.

EXPERIMENTAL

Tests of completeness of coating of walls and particles

For the present argument it is essential to know that a gelatin concentration of 0.01 per cent produces an effective coating on both glass particles and cell wall. While it has been the universal finding that this concentration is sufficient to ensure adequate coating (1, 4, 6), two types of experiments were carried out to test this point.

First, if the cell is allowed to stand filled with 1 per cent gelatin in distilled water for an hour, then rinsed with 0.01 per cent gelatin in distilled water, the ratio is still well above unity; in one case of three the ratio was not altered by previous cell treatment with 1 per cent gelatin, in two cases it was somewhat lowered, presumably because of adventitious factors. Also, in the case of the experiments with 0.02 per cent Eastman gelatin given in table 2 the cell had stood for an hour before the experiment filled with 1 per cent gelatin, yet the ratio is clearly greater than unity. We confirm earlier findings that equilibrium conditions are established within an hour.

Second, simultaneous determinations of electrophoretic and electroosmotic isoelectric points were carried out. If the cell is incompletely coated while the particles are completely coated there will be electroosmotic movement with no electrophoretic movement. A series of 0.01 per cent solutions of Eastman's gelatin was prepared from the same stock solution. All were $2 \times 10^{-4} M$ in added chloride, with various proportions of hydrochloric acid and potassium chloride to vary the pH, which was determined with the glass electrode. The results are shown in figure 1. Plotting u , electroosmotic velocity, and v , electrophoretic velocity, against pH gives smooth curves, both of which cross the axis of zero mobility at pH 4.75.

The objection might be raised that even though a concentration of 0.01 per cent gelatin coats the cell wall sufficiently to make the wall behave as a gelatin surface when at its isoelectric point, the coating may still not be adequate to make the wall behave as a gelatin surface when zeta is other than zero, while the broken particle surfaces would be adequately coated. That is, the advocates of the view that the ratio is always unity, given identical surfaces, might say that our findings are due merely to incompleteness of the cell wall coating as compared with the particle coating. A further reason, however, for believing that the cell wall is in fact completely coated in 0.01 per cent gelatin is the finding of Dummett and Bowden and of ourselves that electroosmotic velocity at constant pH falls as gelatin concentration is increased from zero and becomes constant at a concentration between 0.001 and 0.01 per cent, i.e., the electroosmotic velocity changes from that of bare glass to that of gelatin, the latter being attained at between 0.001 and 0.01 per cent gelatin. The argument must

be confined to completeness of coating of the *cell wall*; it cannot be maintained that the particles are less completely coated than the cell wall, for in that case electrophoretic velocity would be greater than electroosmotic. Monaghan and White (5) found that when one uses microscopic glass particles with fused surfaces the ratio of electroosmotic to electrophoretic velocity is greater than unity in potassium chloride solutions of $10^{-3} M$ or lower concentration. Here we have a case where wall and particle surfaces are known to be identical; the observation has a rather direct bearing on the point under discussion, in that it shows that

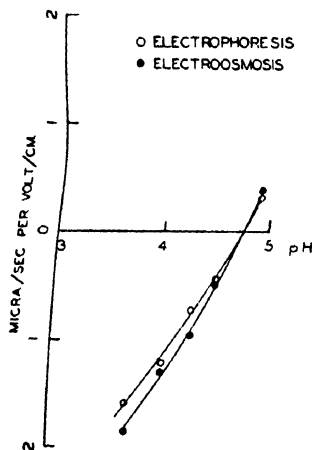


FIG. 1

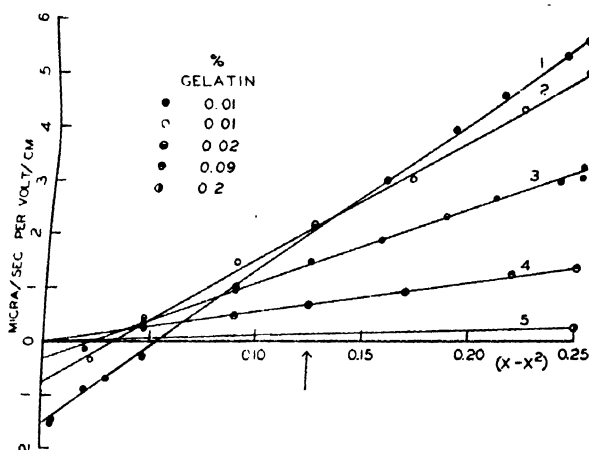


FIG. 2

FIG. 1. pH-mobility curves of electrophoresis and electroosmosis in 0.01 per cent Eastman gelatin, showing identity of isoelectric points.

FIG. 2. Effect of varying gelatin (Eastman) concentration in distilled water on mobilities and ratio of mobilities. The function $(x - x^2)$ of equation 1 is plotted on the horizontal axis. The y intercept shows the excess of electroosmotic over electrophoretic mobility. The arrow indicates the level, $x = 0.147$, of true electrophoretic mobility. The mobility at the center of the cell, where $x - x^2 = 0.25$, is the sum of electroosmotic and electrophoretic mobilities. The numbers of the various curves refer to the experiment numbers of table 1.

it is possible to have a greater than unity ratio with identical surfaces, although it does not directly prove the case for gelatin. The matter seems worth discussing, aside from its purely theoretical implications, because of its rôle in the explanation advanced by White and Monaghan (9) of the common observation that the critical potential (as determined by electrophoresis) seen with electrolytes which coagulate on low concentration is lower than that with those which require higher concentrations; the lower apparent critical potential with the polyvalent electrolytes is considered to be an artifact due to the impossibility of calculating the true zeta potential from electrophoretic mobility in dilute solutions.

Effect of gelatin concentration

We find that varying the gelatin concentration, in distilled water solution, has a very marked effect (table 1 and figure 2). In every case, concentrations of 0.08 per cent or more give low mobilities, and ratios of unity. For concentrations of 0.01 to 0.02 per cent gelatin, except Agfa gelatin, the electroösmotic mobility is the larger, the ratio ranging from 1.13 to 1.78. The spread of values at a given concentration (0.01 per cent) in different experiments must be due to the combination of a number of

TABLE 1
Effect of gelatin concentration in distilled water

EXPT. NO.	GELATIN	<i>c</i>	<i>u</i>	<i>v</i>	<i>R</i>	pH
	<i>grams per 100 cc.</i>	<i>micra per second per volt per cm.</i>				
	Eastman					
1	0.01	1.53	3.57	2.04	1.75	6.32
2	0.01	0.78	2.88	2.10	1.37	
3	0.02	0.32	1.73	1.41	1.23	
4	0.09	0	0.68	0.68	1.00	
5	0.2	0	0.135	0.135	1.00	4.87
	Coignet					
6	0.01	1.82	4.29	2.43	1.76	
7	0.01	1.05	3.52	2.48	1.42	
8	0.01	1.73	3.80	2.20	1.77	6.12
9	0.01	0.70	1.98	1.28	1.55	
10	0.02	0.66	2.32	1.64	1.41	5.59
11	0.1	0	0.64	0.64	1.00	
12	0.2	0.02	0.475	0.45	1.06	5.28
	Agfa					
13	0.01	0	0.45	0.45	1.00	6.80
14	0.02	0	0.20	0.20	1.00	
15	0.05	0	0.07	0.07	1.00	
16	0.1	0	0.06	0.06	1.00	
17	0.2	0	Very slow		1.00	6.21

uncontrolled factors, such as the following: protein concentration itself, within small limits; accidental electrolyte contamination; age and history of the gelatin solution; temperature.

Effect of electrolytes

Table 2 shows that the ratio of the two mobilities is slightly more than unity in 10^{-3} *M* potassium chloride, but is unity in 10^{-2} *M*, confirming the results of White, Monaghan, and Urban (8). Both Coignet and Eastman gelatins, the latter in two concentrations, 0.01 and 0.02 per cent, show this

effect. Comparison of the two gelatin concentrations in each concentration of added electrolyte shows a lower velocity for higher gelatin con-

TABLE 2
Effect of added electrolyte

EXPT. NO.	GELATIN	ADDED KCl	c	u	v	R	pH
	grams per 100 cc.	molar	micra per second per volt per cm.				
	Eastman						
1A	0.01	0	1.60	3.65	2.05	1.78	
1B	0.01	10^{-4}	0.93	2.25	1.32	1.70	
1C	0.01	10^{-3}	0.20	0.99	0.79	1.25	
1D	0.01	10^{-2}	0	0.49	0.49	1.00	
3A	0.02	0	0.32	1.73	1.41	1.23	
3B	0.02	10^{-4}	0.40	1.40	1.00	1.40	5.15
3C	0.02	10^{-3}	0.17	0.77	0.60	1.28	5.00
3D	0.02	10^{-2}	\pm	0.32	0.36	0.92	4.86
	Coignet						
7A	0.01	0	1.05	3.52	2.48	1.42	
7B	0.01	10^{-4}	0.90	3.18	2.28	1.39	
7C	0.01	10^{-3}	-0.43	1.43	1.85	0.77	
7D	0.01	10^{-2}	0	0.72	0.72	1.00	
9A	0.01	0	0.70	1.98	1.28	1.55	
9B	0.01	2×10^{-4}	0.34	1.40	1.06	1.32	
9C	0.01	10^{-3}	0.09	0.74	0.64	1.16	

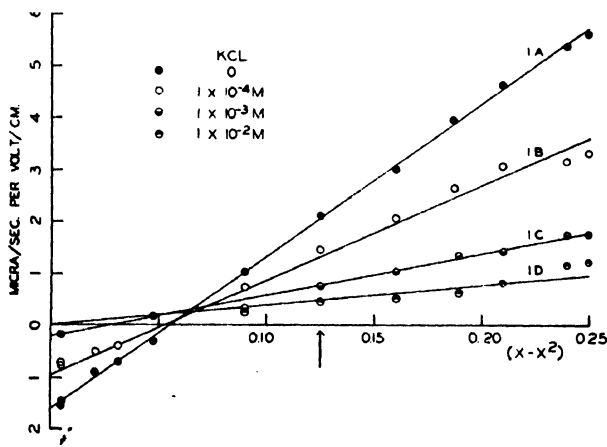


FIG. 3. Effect of varying concentration of added electrolyte on mobilities and ratio of mobilities of 0.01 per cent Eastman gelatin. The numbers of the curves refer to the experiment numbers of table 2.

centration, as did the experiments on gelatin in distilled water. Figure 3 shows straight-line plots of experiments with 0.01 per cent Eastman gelatin.

Differences in the gelatins

Since we did not dialyze any of these preparations, some differences due to the ash content may be expected. The specific conductances of 0.1 per cent solutions of these gelatins were measured in a separate set of experiments, and were found to be 7.67, 30.6, and 36.2×10^{-6} mhos for Eastman, Coignet, and Agfa gelatin, respectively. Neither the makers' stated ash content nor the determined conductivity suffices to account for the low mobility of our sample of Agfa gelatin; it must be attributed to the intrinsic properties of this particular protein.

DISCUSSION

Four of the six experiments on gelatin reported by Moyer and Abramson were done with gelatin concentration of 0.2 per cent, one with 0.05 per cent gelatin, and one with 0.02 per cent gelatin, the last showing the highest value of the ratio found by them, 1.11. Bull's experiments were done with gelatin concentrations ranging from 0.158 to 0.219 per cent, and were all in 3 to 8×10^{-4} *M* hydrochloric acid. Since White, Monaghan, and Urban used a gelatin concentration of 0.01 per cent (Eastman purified gelatin, no dialysis) the present series of experiments shows that there is no incompatibility in the results of the various workers.³ Moyer and Abramson's velocities are expressed only in relative units, and so do not permit a quantitative comparison.

That the reversal near the wall is not due to any specific wall effects, as suggested by Moyer and Abramson to account for their occasional observation of this same phenomenon, is seen from the fact that the value of *c* at the wall is determined not solely by points taken near the wall, but is consistent with mobilities at depths all the way down to the center. The nearest approach to the wall which it is feasible to make is a matter of 0.01 to 0.02 mm., the cell diameter being 2.420 mm.

The present experiments confirm the previous work of White, Monaghan,

³ Since this paper was written Moyer, working in Abramson's laboratory, informs us that he finds that with 0.01 per cent and even with 0.001 per cent gelatin the ratio is usually unity, provided that the particles are first treated with a stronger gelatin solution, and sometimes even without such pretreatment. His interpretation is that when adequate measures are taken to insure complete coating of both surfaces the ratio is unity. We find, on the other hand, the ratio greater than unity with 0.01 per cent gelatin even though both cell and powder have first been treated with 1 per cent gelatin and then allowed to come to equilibrium with 0.01 per cent. It seems to us most probable that differences in the nature or previous treatment of the gelatins must be responsible for the discrepancies of observation; it will be noted that our Agfa gelatin always showed unity ratio even with 0.01 per cent concentration in distilled water. The fundamental question of whether a ratio greater than unity, when it is observed, is due to a real difference in the electrokinetics of electrophoresis and of electroösmosis, respectively, or merely to a lack of identity of surfaces is still not answered to the satisfaction of all concerned.

and Urban in showing the electrophoretic velocity to be lower than the electroösmotic in low gelatin and electrolyte concentrations; they also confirm the work of Bull and of Moyer and Abramson, in finding the velocities the same with higher gelatin but unchanged electrolyte concentration. The essential difference between the two sets of experiments seems to lie in the concentration of gelatin. No satisfactory explanation of the reason for this effect of gelatin concentration is apparent; however, its similarity to that of added inorganic electrolyte suggests that the gelatin, by virtue of its ionization as zwitter ions, is itself the equivalent of added electrolyte. The zwitter-ion electrolyte, although often stated to have the properties of a strong electrolyte, would not be revealed by the conductivity measurements which have usually served as criteria for freedom from electrolytes. The suggestion may be given a rough quantitative test. According to the compilation of Czarnetsky and Schmidt

TABLE 3
Effect of added zwitter ions
0.01 per cent Eastman gelatin in 1×10^{-4} M acetate buffer

ADDED GLYCINE	pH	SPECIFIC CONDUCTIVITY AT 25°C.	u	v	R
molar		mhos $\times 10^5$	micra per second per volt per cm.		
0	5.39	1.57	1.97	1.13	1.74
5×10^{-5}	5.45	1.39	2.19	1.30	1.68
5×10^{-4}	5.35	1.34	2.10	1.50	1.40
5×10^{-3}	5.44	1.40	1.91	1.66	1.15
1×10^{-2}	5.21		1.25	1.05	1.19
5×10^{-2}	5.50		1.65	1.65	1.00
2×10^{-1}		1.15			

(3), the total acid-binding capacity of gelatin is 89×10^{-5} moles per gram; the total base-binding capacity is 64×10^{-5} moles per gram, averaged from conductimetric and potentiometric determinations. These experimentally determined values agree roughly with those calculated by them from the known amino acid composition. On this basis, at the isoelectric point there are present 64×10^{-5} moles of zwitter ions per gram of gelatin, and a 0.1 per cent solution is 6.4×10^{-4} molar in zwitter-ions, at a maximum. Since the concentration of potassium chloride required to bring the ratio of the two velocities to unity falls between 10^{-3} and 10^{-2} molar, it is evident that if the gelatin is acting as a zwitter-ion electrolyte, it is either about twice as effective as is potassium chloride, or it has an additional effect of some other nature.

In order to test experimentally the concept that zwitter ions may affect electrophoretic mobility, the influence of added glycine in various concentrations on the ratio of electroösmotic to electrophoretic mobility of

0.01 per cent Fastman gelatin was determined. The values of u and v in this series were determined by observations at the 50 and 14.7 per cent cell diameter levels. The findings are shown in table 3. It is evident that added glycine, although it has no significant effect on conductivity of the solutions employed, acts as does added potassium chloride in lowering the ratio to unity. The supposition is thus strengthened that the unity ratio seen in high gelatin concentrations, as 0.1 or 0.2 per cent, is due to the same mechanism.

SUMMARY

Evidence is presented that 0.01 per cent gelatin is sufficient to coat completely the suspended particles and cell wall, giving characteristic protein surfaces; our former finding is confirmed that here the ratio is greater than unity in potassium chloride solutions of concentration $10^{-3} M$ or lower.

Evidence is presented that the ratio of electroösmotic to electrophoretic mobility is dependent on the concentration of gelatin as well as of added electrolyte.

The effect of added gelatin is qualitatively the same as that of added electrolyte and is apparently due to its zwitter-ion concentration.

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THE INTERACTION BETWEEN PROTEINS AND FATTY ACIDS ON THE SURFACE OF AQUEOUS SOLUTIONS^{1,2}

HANS NEURATH³

Department of Chemistry, Cornell University, Ithaca, New York

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The problem of the interaction between proteins and lyophobic substances seems to be of interest in regard to the structure of proteins, since it bears upon the function of the lyophilic and lyophobic groups as well as on the structure of certain biological systems which consist mainly of proteins and such lyophobic materials as fats and lipids. The membranes of the living cells are examples of such systems, and their structure and function depend not only on the chemical composition but to a large extent also on the orientation of the individual compounds on the surface. A relatively easy way of studying such systems is provided by the method of spreading in surface films, inasmuch as proteins in the cell membranes as well as on the surface of aqueous solutions are probably present in the surface-denatured state (6). Such studies have been carried out recently by Hughes (7) and by Schulman and Hughes (10). Their investigations differ essentially, however, from those described in this paper, in that they studied the phenomenon of "film penetration" by injecting the protein underneath a film of fatty acids and similar materials, whereas in these experiments proteins and the lyophobic material were spread simultaneously in order to ascertain complete spreading. In order to deal with relatively simple and well-defined systems, instead of fats and lipids, fatty acids such as stearic acid, palmitic acid, or myristic acid were chosen for these studies. Of these acids only myristic acid gave satisfactory results under the conditions of spreading used.

The experiments reported below are to be regarded as preliminary; publication at the present stage seemed desirable, however, as many data have been accumulated and a partial analysis of the problem accomplished.

¹ Presented at the Fourteenth Colloid Symposium, held at Minneapolis, Minnesota, June 10-12, 1937.

² The experimental part of this paper was carried out in 1934-35 at the University College, London, England. The author is greatly indebted to Professor F. G. Donnan, F.R.S., for his hospitality and for his interest in these investigations.

³ George Fisher Baker Research Fellow.

EXPERIMENTAL

A. Preparation of solutions

Ovalbumin solutions were prepared in exactly the same manner as described in the previous paper (8), i.e., by separating the yolk of fresh hens' eggs from the white, diluting the latter with distilled water, and filtering off the precipitated globulins. The filtrate was electrodialedyzed in Pauli's apparatus (9) for several days, the voltage being gradually increased from 5 to 220 volts. After seven days the conductivity had reached its minimal value of $81 \cdot 0^{-5}$ mhos with 2 per cent protein solution (pH 4.80).

Aqueous solutions of fatty acid were prepared by dissolving the acid first in a minimal volume of 96 per cent ethyl alcohol and adding to this solution dilute potassium hydroxide until a water-clear solution resulted. This soap solution was spread on *N*/10 hydrochloric acid, thus forming a film of the free fatty acid on the surface. When using palmitic acid it was found that homogeneous films of the fatty acids could not be obtained under any circumstances, the area per molecule yielding values of 12 to 13 sq. A. U. instead of the theoretical value of 20.5 sq. A. U. at zero compression. Likewise, when using the choline salt of palmitic acid, which is more soluble in water than the potassium salt, the area per molecule of fatty acid was reduced to 18 sq. A. U.

When using the potassium salt of myristic acid it was found that the area per molecule of fatty acid depended, as in the former case, on the amount of potassium hydroxide added to the alcoholic solution of the myristic acid. In all instances the myristic acid was dissolved in 5 cc. of ethyl alcohol and diluted with potassium hydroxide to 100 cc. With a mole ratio of potassium hydroxide to myristic acid of 4:1 the area per molecule of fatty acid amounted to 38 to 42 sq. A. U. at zero compression. A mole ratio of 2:1 yielded an area of 41.5 to 47 sq. A. U., and a mole ratio of 1.2:1 an area of 51 to 52 sq. A. U., in good agreement with the theoretical value. The transition from the expanded to the condensed state occurred at an area of 31.5 sq. A. U., which is 0.5 sq. A. U. smaller than the theoretical value. All results refer to 18.0°C.

Mixtures of protein and fatty acid were prepared by adding to the solution of potassium myristate which contained 5 per cent alcohol (mole ratio of potassium hydroxide to myristic acid = 1.2:1) varying amounts of ovalbumin solution. The total volume of the mixture was always 5 cc. The concentration of ovalbumin and potassium myristate was adjusted in such a way that about 0.05 to 0.08 cc. of the solution when spread yielded a film which almost covered the free surface of the trough.

B. Measurements

The apparatus of Adam and Jessop (3) was used. The films were frequently examined by the dark-ground illumination introduced by Zocher

and Stiebel (11) and with the simplification used by Adam (1). A brass trough was used, and the temperature regulated by an electrical heater below the trough. The technique was essentially the same as described in the previous paper (8). The solutions were spread from an Agla micrometer syringe, capable of being read to 0.0001 cc. Complete spreading was attained 15 min. after the material had been put on the surface of a solution of $N/10$ hydrochloric acid. All measurements quoted below are the mean of seven to ten readings.

RESULTS

Experiments on the spreading of isoelectric ovalbumin on $N/10$ hydrochloric acid showed that the properties of the films deviated only slightly

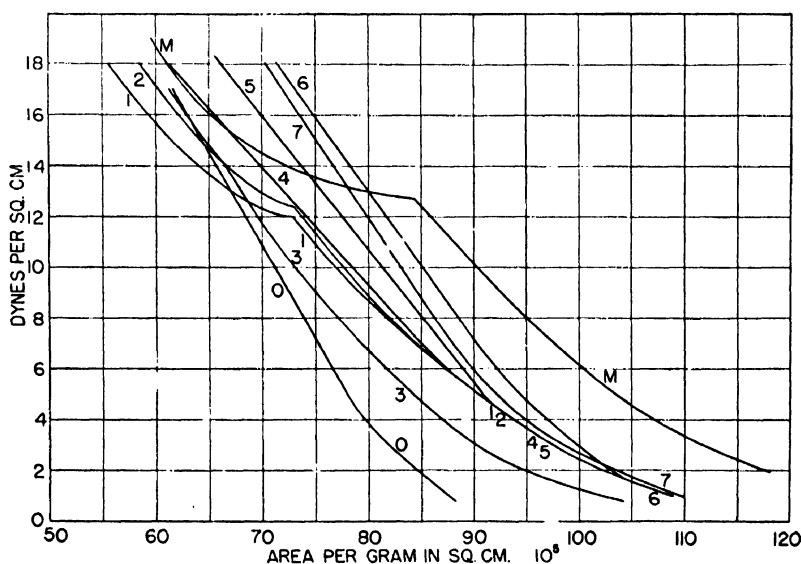


FIG. 1. Spreading of potassium myristate, ovalbumin, and mixtures of both on $N/10$ hydrochloric acid. Curve O, ovalbumin; curve M, potassium myristate; curve 1, mole ratio of potassium myristate to ovalbumin 393; curve 2, mole ratio 247; curve 3, mole ratio 97.5; curve 4, mole ratio 67.5; curve 5, mole ratio 30.7; curve 6, mole ratio 17.8; curve 7, mole ratio 9.

from those of previous investigations. The area per molecule at zero compression was 5600 sq. A. U., whereas it amounted to 5000 sq. A. U. when the protein was spread on $N/20$ acetate buffer (pH 4.8). Collapsing started at a pressure of 15 dynes per centimeter, 3 dynes lower than when spread on acetate buffer. The slope of the straight part of the pressure-area curve was 72 sq. A. U. per dyne or 1.29 per cent of the area at zero compression, as compared with 70.5 sq. A. U. per dyne or 1.41 per cent of the area at zero compression when spread on acetate buffer.

Figure 1 shows the pressure-area curves of pure myristic acid, of pure

ovalbumin, and of mixtures of both. Plotted as ordinates are the surface pressures in dynes per centimeter and as abscissae the surface areas per gram of solute in square centimeters $\times 10^{-5}$. Table 1 illustrates the composition and the properties of the films.

There appear two distinct changes in the properties of the films as the relative amount of myristic acid in the mixtures decreases. The inflection point, which in the case of pure myristic acid marks the transition from the liquid-expanded to the condensed state, disappears, and whereas at high relative concentrations of myristic acid the films are in the liquid state throughout the whole pressure range, with decreasing relative

TABLE 1
Mixed films of myristic acid and ovalbumin

CURVE NO.	PER CENT OF MYRISTIC ACID PER GRAM OF MIXTURE	MOLE RATIO OF MYRISTIC ACID TO OVALBUMIN	TOTAL AREA PER GRAM OF MIXTURE IN CM. ² $\times 10^{-5}$			INFLECTION POINT AT DYNES	PROPERTIES OF FILMS
			2 dynes	5 dynes	10 dynes		
M.	100		118	103.5	90	12.6	Liquid
1.	72.2	393	102.5	91	77.6	12	Liquid
2.	43.6	247	102.5	90.5	77.7	12.3	Liquid
3.	39.3	97.5	95	84.3	73.2	17.4	Liquid
4.	30.9	67.5	103	91	78.5	No inflection point	Slightly elastic, rigid
5.	16.9	30.7	102	91.1	81.5	No inflection point	Elastic and solid above 5 dynes
6.	10.5	17.8	103.5	95	85	No inflection point	Elastic and solid above 5 dynes
7.	5.6	9	104	92	83	No inflection point	Elastic and solid above 5 dynes
0.	0	0	84.5	73	71	No inflection point	Elastic and solid above 4 dynes

amount of fatty acid they assume gradually the solid type which is characteristic for the pure protein film.

DISCUSSION

Whereas a plot as illustrated in figure 1 does not reveal any regularity of the behavior of the individual compounds, a deeper insight into the mechanism of the mutual interaction between the two compounds can be gained when it is assumed that the surface of either one of the compounds remains unaltered by the addition of the other.

Figure 2 illustrates the extrapolated pressure-area curves of myristic acid, calculated on the basis that the area of ovalbumin was unchanged by the addition of the fatty acid. From each curve of figure 1 the values

of the total area per gram were read off at about twenty different pressures and the area per molecule of myristic acid calculated, taking into account the change of the area of ovalbumin with pressure. *Vice versa*, the area per molecule of protein was computed in the same manner, assuming that the surface area of the fatty acid remained unchanged by the addition of the protein. This is illustrated by figure 3.

Figure 3 reveals a marked decrease of the area of the protein upon addition of a large excess of fatty acid. Such a decrease seems rather improbable, since the molecule cannot occupy less area than it does in the condensed film of the pure substance. Assuming that in the condensed state the lyophobic groups of the polypeptide chain are oriented perpendicular to the surface, which is in keeping with the results of x-ray analysis (5), an increase of the surface area of the protein would be con-

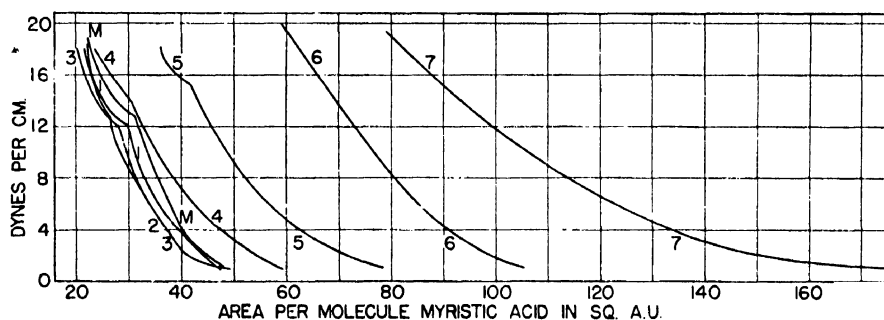


FIG. 2. Extrapolated curves of area per molecule of myristic acid, based on the assumption that the area of the protein remains unchanged by the addition of the fatty acid. Curve M, myristic acid without addition of ovalbumin; curve 1, mole ratio of myristic acid to protein 393; curve 2, mole ratio 247; curve 3, mole ratio 97.5; curve 4, mole ratio 67.5; curve 5, mole ratio 30.7; curve 6, mole ratio 17.8; curve 7, mole ratio 9.

ceivable only either by tilting of the molecule about the polypeptide chain or by decreased lateral adhesion between neighboring molecules. The curves of figure 3 reveal also a sharp break, which is preceded by a flattening out and followed by a sharp *increase* of the area with increasing pressure. Such a shape of pressure-area curves seems rather improbable and is without precedent in the literature.

There is, on the other hand, strong evidence for the assumption that the molecules of the fatty acid will be influenced by the large and rather compact molecules of the protein film. Figure 2 shows that with mole ratios of fatty acid to protein of 393, 247, and 97.5, respectively, the area per molecule of myristic acid is somewhat decreased. This decrease is probably due to a condensing effect, which has been observed by Adam and Jessop (4) for mixtures of cholesterol and myristic acid and which has been

ascribed to a prevention of the spreading of myristic acid by the large and rather inert molecules of cholesterol. In our case this condensing effect is very small and indicates the absence of any special attraction between the molecules of the protein and of the fatty acid at these concentrations. The change from the solid state when the protein is spread alone, to the liquid state when the acid is present is noteworthy and prob-

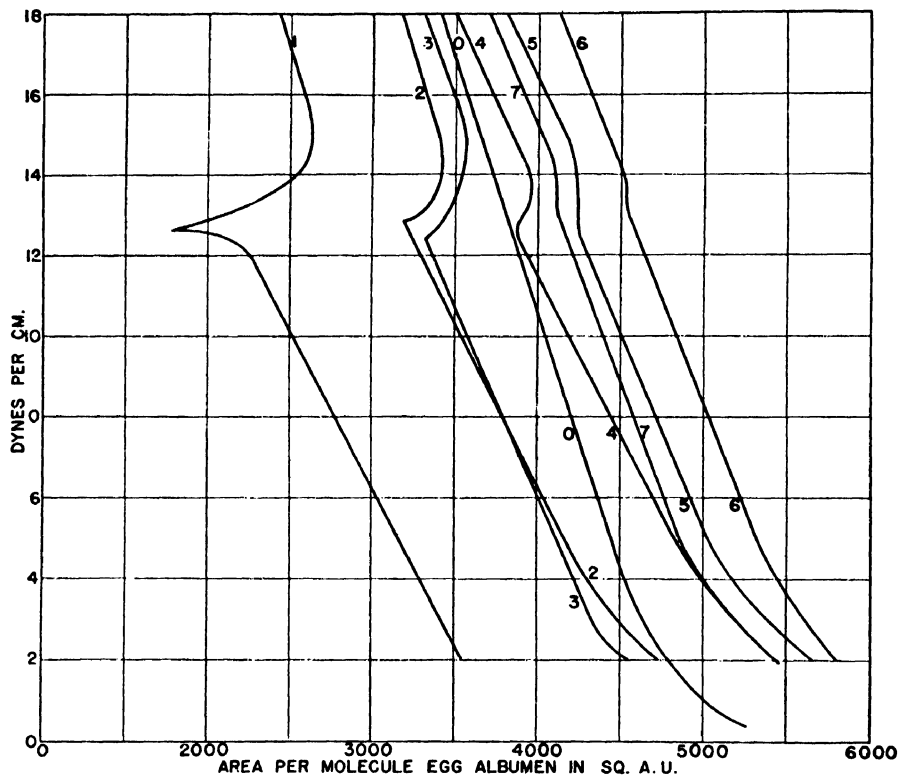


FIG. 3. Extrapolated curves of area per molecule of ovalbumin, based on the assumption that the area of the fatty acid remains unchanged by the addition of the protein. Curve 0, ovalbumin without addition of myristic acid; curve 1, mole ratio of myristic acid to ovalbumin 393; curve 2, mole ratio 247; curve 3, mole ratio 97.5; curve 4, mole ratio 67.5; curve 5, mole ratio 30.7; curve 6, mole ratio 17.8; curve 7, mole ratio 9.

ably due to slight changes of the lateral adhesion between neighboring molecules.

With mole ratios smaller than 97.5 a marked increase of the area of myristic acid sets in which, with a mole ratio of 9, assumes values of more than 180 sq. A. U. at zero compression. This increase is accompanied by a gradual increase of the compressibility of the films as revealed by the flattening out of the curves at low pressures (curves 5, 6, and 7 of figure 2).

Furthermore, within this range of concentration the curves do not show a transition from the expanded to the condensed state and do not tend to a definite limiting area at zero compression. These facts as well as the large areas, which could not be accounted for even if the molecules lie flat on the surface, suggest that with low relative concentrations of myristic acid the films are in the liquid-expanded and vapor-expanded state, respectively.

In general, the extent of lateral adhesion between the molecules determines whether a film is expanded or condensed. For a given chain length of a fatty acid, for instance, the lateral adhesion between the end groups can be enormously decreased when the end groups become ionized. Thus, acids form gaseous films on alkaline solutions, whereas on acid solutions they are in the liquid-expanded and condensed state (Adam (2)).

This decrease of lateral adhesion between the end groups could be brought about not only by electrical repulsion between ionized groups but likewise by attractive forces acting between certain groups of the protein and the unionized groups of the fatty acid, which would tend to pull the latter apart (ion-dipole forces). Since the films are spread on an acid solution it is reasonable to assume that the protein will possess only positively charged groups, which presumably are the centers of attraction for the carboxyl groups of the fatty acid. The resultant effect will, as a first approximation, depend on the amount of lateral adhesion between the hydrocarbon chains of the fatty acid and on the amount of attraction between the positively charged groups of the protein and the carboxyl groups of the fatty acid. If no interaction between the hydrocarbon groups of the fatty acid and those of the protein takes place, the first effect should be independent of the relative amount of fatty acid present. The second effect, however, will increase with decreasing relative amounts of fatty acid since, the number of positively charged groups per molecule protein being limited, only a certain number of fatty acid molecules can react electrostatically with each protein molecule, whereas the rest will be unaffected.

Such an hypothesis concurs with the experimental findings: At high relative concentrations of myristic acid the films are coherent and no considerable interaction takes place. As the relative amount of myristic acid decreases, a competition between the adhesive forces of the hydrocarbon chains of the fatty acid and the attractive forces between the end groups of the latter and the positively charged groups of the protein sets in which, with a large excess of protein, leads to a state where the molecules of the fatty acid are neither upright nor lying flat on the surface but are in a vibratory motion between these two extremes of orientation. The total effect would be a gradual change from the liquid-expanded to the vapor-expanded or gaseous state. The fact that with low concentrations of the fatty acid the films are solid would not necessarily contradict

this view; it would be conceivable that the vapor-expanded or gaseous film of the fatty acid is imbedded in the rigid structure of the protein film. This hypothesis is, of course, only suggestive, and its proof has to await further work along this line.

SUMMARY

As a preliminary study of the problem of the interaction between proteins and lyophobic substances, the behavior of ovalbumin and fatty acids on the surface of aqueous solutions has been studied.

Mixed films of ovalbumin and myristic acid have been prepared by spreading a solution of potassium myristate and ovalbumin on the surface of *N*/10 hydrochloric acid. If it is assumed that the protein occupies the same area as in the pure film of that substance, no appreciable interaction between the two compounds could be found with films containing between about 400 and 100 molecules of myristic acid per molecule of protein. With films containing less than 100 molecules of myristic acid, a marked increase of the area per molecule of fatty acid sets in which, with a mole ratio of 9, reaches a value of more than 180 sq. A. U. The hypothesis has been advanced that within this range of concentration the films are in the vapor-expanded or gaseous state, owing to a sharp decrease of the lateral adhesion between the molecules of the fatty acid. This decrease of the lateral adhesion is presumably brought about by attractive forces acting between the carboxyl groups of the fatty acid and the positively charged groups of the protein film.

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THE EFFECT OF ROENTGEN RAYS ON THE COLLOIDAL PROPERTIES OF ERYTHROCYTES¹

HELEN QUINCY WOODARD

Memorial Hospital, New York City, New York

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INTRODUCTION

In a recent address Failla (2) advanced a theory of the action of penetrating radiation on living material. The theory is based on the observation that both the cells of irradiated tissue and their nuclei swell following exposure to Roentgen rays or to the alpha, beta, or gamma rays of radium. It is known that radiation of these types ionizes matter, producing "radio ions." These are "atoms, molecules, or aggregates which either have lost or have acquired electrons." They are distinct from ordinary chemical ions, and usually recombine rapidly by exchange of an electron. They may, however, regroup themselves with the formation of new chemical substances. If this latter process takes place inside a living cell, and if the new substances have a smaller molecular weight than the parent substances, the osmotic pressure inside the cell will increase. If the intercellular fluid, such as blood or lymph, is affected to a less extent than the cell contents, or if it is replaced with unchanged fluid by the circulation, the cells will swell. Direct injury to the cell membrane would intensify this effect by weakening the resistance of the membrane to the increased internal pressure.

It is difficult to test this theory with cells imbedded in a slowly permeable stroma, such as those in the intact organism or in tissue culture. Of isolated cells the most readily available are mammalian erythrocytes. These are undesirable because of their well-known high radioresistance. On the other hand, since they are non-nucleated, they are free from the complications which might be introduced by the presence of a second osmotic system within the first. Accordingly, suspensions of washed sheep erythrocytes were chosen for the present study.

Since it was found that hemolysis played an important part in the phenomena observed, it will be convenient here to review the mechanism of this process. When erythrocytes are placed in hypotonic solutions they swell in accordance with osmotic laws (4, 7). There is at first no

¹ Presented at the Fourteenth Colloid Symposium, held at Minneapolis, Minnesota, June 10-12, 1937.

change in the permeability or electrical properties of the membrane (3). When the membrane has been stretched to a critical degree, however, it suddenly becomes completely permeable to hemoglobin, about 90 per cent of which then escapes into the surrounding medium in less than 1 sec. (9). The electrical properties of the membrane change at the moment of hemolysis, but the membrane persists unruptured as a "ghost." If the hemolyzed ghosts are then placed in hypertonic solutions they shrink like normal erythrocytes and regain most of their former osmotic and electrical resistance (9). The permeability of the membrane in hypotonic hemolysis is nearly constant regardless of the tonicity of the solution used to bring about the hemolysis (9).

When hemolysis is brought about by a lysin such as saponin, instead of by exposure to hypotonic solutions, the primary effect is on the membrane rather than on the contents of the cell. As in hypotonic hemolysis, the cell hemolyzes completely or not at all. However, after hemolysis by saponin the cell membrane is irreparably damaged, does not recover its former properties, and may disappear altogether (3).

Although the hemolysis of the individual erythrocyte is an "all or none" process, the hemolysis of any given sample of blood is not, because the red cell population is a heterogeneous one showing all degrees of resistance. Hence it is possible by appropriate treatment to hemolyze any fraction of a sample of cells from zero to 100 per cent. Since hemoglobin solutions obey Beer's law (1), the per cent of hemolysis is readily determined by means of photoelectric readings on the supernatant liquid obtained by centrifuging a partly hemolyzed suspension.

METHOD

Preliminary work was done on heparinized blood in order to avoid possible osmotic effects from a small molecule anticoagulant such as oxalate. Heparin did not prove a satisfactory anticoagulant for large volumes, however, so, as no difference was detected in the behavior of washed cells from oxalated and heparinized samples, oxalated blood was used in most of the work. Sheep blood containing 2 mg. of potassium oxalate per cubic centimeter was obtained in 300-cc. lots fresh from the slaughter house. It was centrifuged at once, the plasma pipetted off, and the cells decanted from the potassium oxalate precipitate and washed three times with 0.9 per cent sodium chloride solution. The cells were then suspended in such a quantity of 0.9 per cent sodium chloride solution that, when packed, they would occupy about 50 per cent of the volume of the suspension. The suspension was kept in the ice box until used.

Before being irradiated the suspension was placed in 1-cc. hematocrit tubes closed with vaccine stoppers and centrifuged at a force of $1000 \times$ gravity. Forty-five minutes was required for the packed cells to come to

constant volume at this centrifugal force. The sodium chloride solution was then removed, the tubes re-stoppered, placed in a cardboard box, and irradiated. Sodium chloride solution of the desired concentration was then added, the cells redispersed by shaking, and the tubes kept in a horizontal position in the ice box for seventeen to twenty hours. They were then re-centrifuged, and the cell volume read with a precision of about ± 0.5 per cent.

The per cent hemolysis was determined by photoelectric readings on the supernatant liquid in the hematocrit tubes. Reference values for 100 per cent hemolysis were obtained by centrifuging tubes of stock suspension, removing the saline, and adding distilled water. Owing to the high opacity of the completely hemolyzed preparations there was a possible error of 10 per cent in these photoelectric readings. The error in reading the partially hemolyzed preparations was proportionately less, so that, although all the determinations in a given experiment were subject to the possible error in the 100 per cent value, they were consistent among themselves to a higher precision than that of the 100 per cent standard. As Roentgen irradiation colors the glass of the hematocrit tubes, blank readings were always made on tubes of the same color as the experimental ones.

Several investigators (5, 6) have shown that hemolysis is profoundly influenced by temperature. It was impossible in the present work to maintain a constant temperature throughout the course of an experiment. Hence great care was exercised to avoid temperature differences between irradiated and control tubes during manipulation.

The Roentgen rays were obtained from a mechanically rectified machine with water-cooled tube having glass walls 4 mm. thick. It was operated at 200 kv. and 30 ma.; distance from target to hematocrit = 40 cm.; filter = 1 mm. glass + 1 mm. cardboard; intensity = 270 r. per minute; dose = 16,200 roentgens. This dose is much greater than any which would be tolerated by the intact organism, but previous experience by the author and many others has shown that material irradiated *in vitro* is usually highly radioresistant.

RESULTS

Preliminary work indicated that, when whole sheep blood was irradiated, or when centrifuged cells were irradiated alone and unirradiated plasma added, the irradiated cells swelled slightly. This is in accord with Failla's theory. When plasma was irradiated and then added to unirradiated cells, no significant change in the volume of the cells was found. This may indicate either that there is a differential effect on the cell proteins or that changes produced by irradiation in the less concentrated plasma proteins are too small to produce osmotic effects greater than the experi-

mental error. It was apparent at once, however, that much larger effects could be produced by equilibrating the irradiated cells with sodium chloride solutions. This is to be expected from the Donnan relations. Hence most of the work was done with cells equilibrated with salt solutions.

As the effects of irradiation on fresh and aged blood differed markedly, the changes which took place in the control suspensions with time will first be outlined. Figure 1 shows changes taking place in two stock suspensions of washed cells which were kept in 0.9 per cent sodium chloride solution in the ice box. The volume of the cells as shown by the hem-

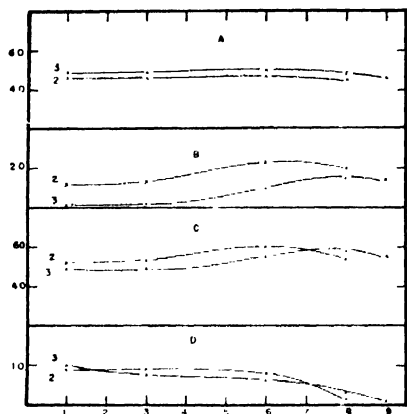


FIG. 1

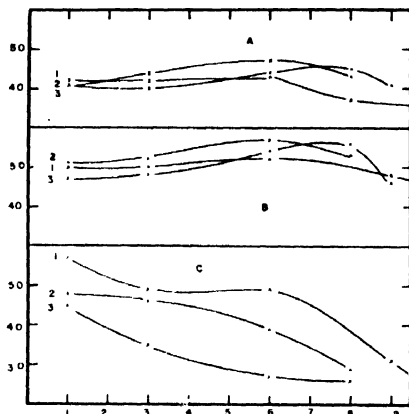


FIG. 2

FIG. 1. Changes in stock suspensions with time. Abscissae = age in days. Ordinates: A = absolute cell volume from hematocrit readings; B = per cent hemolysis; C = specific cell volume; D = photoelectric readings on completely hemolyzed samples.

FIG. 2. Changes with time in the absolute cell volume of unirradiated cells equilibrated with fresh sodium chloride solutions. Abscissae = age in days of cells when fresh solutions were added. Ordinates = absolute cell volume from hematocrit readings. Curves in A, cells in 1.8 per cent sodium chloride; curves in B, cells in 0.9 per cent sodium chloride; curves in C, cells in 0.6 per cent sodium chloride.

atocrit readings remains approximately constant over a period of several days. The degree of hemolysis, on the other hand, increases rather suddenly after a variable period of time which, for the samples shown, was about six days. If the specific cell volume is calculated by the formula,

$$\text{specific cell volume} = \frac{\text{absolute cell volume}}{100 - \text{per cent hemolysis}}$$

it is seen that the volume of the remaining intact cells increases. At the same time the light absorption of the hemoglobin in samples completely hemolyzed by the addition of distilled water increases, as is shown by the

drop in the curves for the photoelectric cell readings. The dotted portions of the curves indicate regions in which the photoelectric readings on the completely hemolyzed samples were so small that calculations of per cent hemolysis were subject to large errors. These changes suggest that a spontaneous change takes place in the cell contents which results in an increased intracellular osmotic pressure. This causes the cells to swell, and brings about the hemolysis of those in which the process is most pronounced. In the samples illustrated, the relative rates of swelling and hemolysis were such that the total volume of the unhemolyzed cells remained approximately constant until near the end of the period of observation.

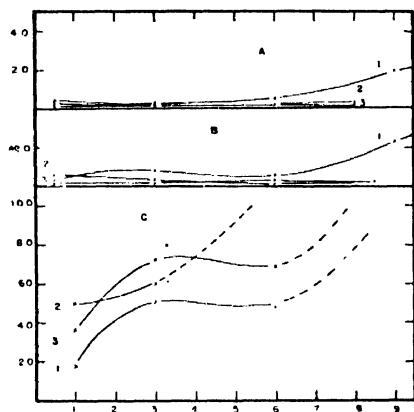


FIG. 3

FIG. 3. Changes with time in the per cent hemolysis of unirradiated cells equilibrated with fresh sodium chloride solutions. Abscissae = age in days of cells when fresh solutions were added. Ordinates = per cent hemolysis. Curves in A, cells in 1.8 per cent sodium chloride; curves in B, cells in 0.9 per cent sodium chloride; curves in C, cells in 0.6 per cent sodium chloride.

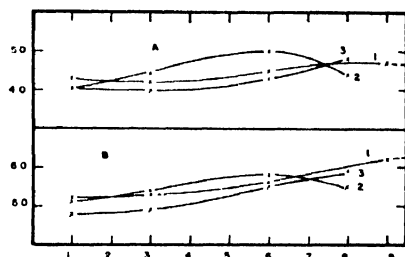


FIG. 4

FIG. 4. Changes with time in the specific cell volume of unirradiated cells equilibrated with fresh sodium chloride solutions. Abscissae = age in days of cells when fresh solutions were added. Ordinates = specific cell volume. Curves in A, cells in 1.8 per cent sodium chloride; curves in B, cells in 0.9 per cent sodium chloride.

When samples of such suspensions are removed from time to time, centrifuged, the old saline removed, and the cells equilibrated for eighteen hours in the ice box with hypertonic, isotonic, and hypotonic sodium chloride solutions, curves like those in figures 2, 3, and 4 are obtained. The absolute cell volume, per cent hemolysis, and specific cell volume are plotted against days of age of the cells when placed in fresh saline. Curves No. 2 and 3 are for the same suspensions as those illustrated in figure 1, and the cell volumes are corrected for losses from hemolysis in the stock suspension. Data were not complete on the hemolysis, which was small, in the stock suspension for curve No. 1, and the cell volumes for this prepara-

tion are uncorrected. In these preparations the cells which were shown by calculation of the specific cell volume in the stock suspension to be somewhat swollen were unable to withstand the further swelling caused by hypotonic solutions, and hemolyzed so extensively that the absolute volume of the intact cells fell rapidly. The specific volume of the cells in hypotonic saline was found to rise very rapidly with increasing age of the cells, but the experimental error of both hematocrit and photoelectric readings is so large in this range that calculations of specific cell volume are without quantitative significance, and are not shown in the chart. On the other hand, if cells of the same lot were placed in isotonic saline, they underwent some additional increase in volume, but this was not sufficient to cause much hemolysis. Cells placed in hypertonic saline, while they shrank somewhat less than they did when fresh, nevertheless diminished somewhat in volume and hemolyzed only very slightly. If the preparations were observed still longer, a marked increase in the light absorption of hemoglobin was found to take place in sodium chloride solutions of all concentrations, the absolute cell volume decreased, and hemolysis finally became complete. Numerous other samples of erythrocytes were found to behave in the same way as those illustrated, although the changes outlined took place at different ages in the different samples.

If the changes induced by irradiation are due to a change in the state of aggregation of the cell contents, it is to be expected that the effect of irradiation of fresh and old cells will be different. This is found to be the case, as is shown in figures 5, 6, and 7. The percentage change in absolute and specific cell volumes and the absolute change in per cent hemolysis are plotted against age of blood sample at the time of irradiation. It is seen that, when *fresh* cells are irradiated and then equilibrated with sodium chloride solutions of different concentrations, the hemolysis undergone by the irradiated cells is always greater than that of the controls. Because of the pronounced hemolysis of irradiated cells suspended in hypotonic saline the absolute volume of the remaining cells is less than that of the controls, while that of the less hemolyzed irradiated cells in isotonic saline undergoes little change, and that of irradiated cells in hypertonic saline remains greater than that of the controls. The specific volume of all the cells irradiated when fresh is greater than that of the controls. As the cells age, however, these relationships change, so that in the oldest preparations the hemolysis of the irradiated cells is less than that of the controls. This reversal of radiosensitivity takes place at approximately the same age as the most marked increase in the light absorption of the hemoglobin.

It appears therefore that irradiation of fresh packed sheep erythrocytes results in the splitting of the hemoglobin to compounds of smaller molecular weight. This causes the cells to swell relatively to the controls when subsequently placed in sodium chloride solutions, and to hemolyze when

the swelling is great enough. This is in accord with the theory of Failla. As the cells age, however, a spontaneous change takes place in the cell

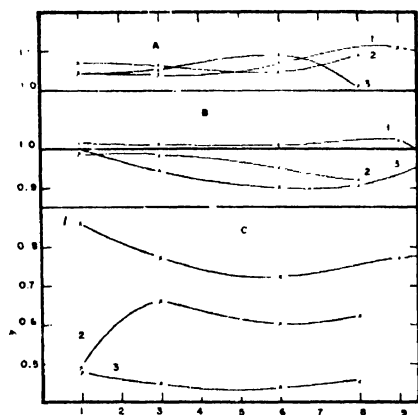


FIG. 5

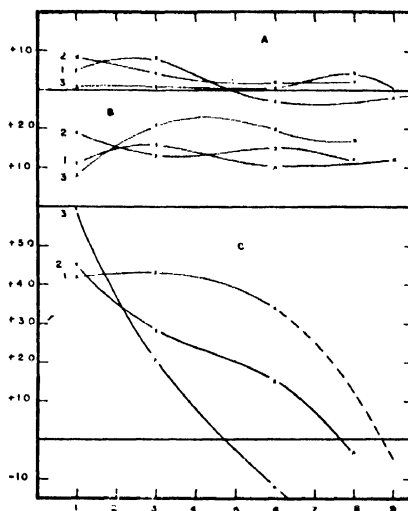


FIG. 6

FIG. 5. Changes in radiosensitivity with time. Abscissae = age in days of cells when irradiated. Ordinates = absolute volume of irradiated cells/absolute volume of control cells. Curves in A, cells in 1.8 per cent sodium chloride; curves in B, cells in 0.9 per cent sodium chloride; curves in C, cells in 0.6 per cent sodium chloride.

FIG. 6. Changes in radiosensitivity with time. Abscissae = age in days of cells when irradiated. Ordinates = per cent hemolysis of irradiated cells minus per cent hemolysis of control cells. Curves in A, cells in 1.8 per cent sodium chloride; curves in B, cells in 0.9 per cent sodium chloride; curves in C, cells in 0.6 per cent sodium chloride.

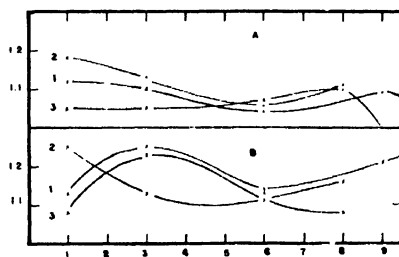


FIG. 7. Changes in radiosensitivity with time. Abscissae = age in days of cells when irradiated. Ordinates = specific volume of irradiated cells/specific volume of control cells. Curves in A, cells in 1.8 per cent sodium chloride; curves in B, cells in 0.9 per cent sodium chloride.

contents which causes the cells to swell. Irradiation of these swollen cells reduces their volume, probably through coagulation of the altered hemoglobin. No evidence is at hand at present as to the nature of the

spontaneous change in the hemoglobin which results in a reversal of the radiation effect. Preliminary work in which the catalase of the cells was inactivated with sodium chlorate indicates that methemoglobin formation may play a part.

No mention has been made of the possible effect of radiation on the cell membrane. The data are more in harmony with the theory that the major portion of the irradiation effect is on the cell contents. It is hoped that direct evidence on this question may be obtained by a study of the radio-sensitivity of cells whose membranes have been weakened by a lysin.

Since the sensitivity of cells which have been irradiated while packed and almost free from saline and then suspended in saline of different concentrations is the same within the experimental error as the sensitivity of these cells when they have been suspended in the corresponding saline solutions just prior to irradiation, it is obvious that the effect of the radiation is on the cells themselves rather than on the medium.

SUMMARY

The effect of 200 kv. Roentgen radiation on the osmotic properties of sheep erythrocytes has been studied.

The volume and the susceptibility to hemolysis of erythrocytes which were irradiated when fresh was increased by irradiation. This effect was reversed when the cells were irradiated after they had been kept in physiological saline for several days at low temperatures.

This is interpreted as meaning that the hemoglobin of fresh cells is split to compounds of smaller molecules by Roentgen radiation, while that of aged cells is coagulated.

The author wishes to express her thanks to Dr. G. Failla for suggesting the problem, and to Mr. John Sachs for technical assistance.

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VIRUS PROTEINS—A NEW GROUP OF MACROMOLECULES¹

W. M. STANLEY

The Rockefeller Institute for Medical Research, Princeton, New Jersey

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INTRODUCTION

Although observations of preparations that were undoubtedly colloidal solutions were recorded over a hundred years ago, it is generally regarded today that colloidal chemistry came into being in 1861 when Graham (15) attempted to divide substances into two classes which he called crystalloids and colloids, respectively. Graham's crystalloids were substances which tended to form crystals on coming out of solution and which diffused readily through a membrane, while his colloids were substances which tended to separate out as amorphous masses and which would not diffuse through a membrane. The crystalloids were generally regarded as molecules and the colloids as particles consisting of aggregates of molecules. The molecules have ranged from fractions of a millimicron up to about 1 or 2 $m\mu$ in diameter and the colloids from several hundred millimicrons down to about 2 $m\mu$ in diameter. Because of the lack of knowledge of macromolecules, colloid chemistry has been built chiefly around work on small particles of gold, silver, mastic, etc., each particle consisting of a great number of molecules. Probably for this reason the idea gradually developed that solutions of such particles were quite different from solutions of molecules and hence that colloidal solutions were different from "true" solutions. However, in 1905 Einstein (11) pointed out that according to the kinetic theory there should be no difference between a suspended particle and a molecule of the same size and that the laws based on the kinetic theory should apply to colloidal solutions in much the same way that they apply to "true" solutions. He considered that colloidal solutions should exhibit such phenomena as osmotic pressure and diffusion and that an equilibrium between the force of gravity and diffusion might be expected. These theoretical considerations were immediately put to experimental test, first by Perrin (30) in 1908 and later by Svedberg (43), Westgren (49), Zsigmondy (55), and others. These workers used colloidal solutions of gold, silver, platinum, selenium, gam-

¹ Presented at the Fourteenth Colloid Symposium, held at Minneapolis, Minnesota, June 10-12, 1937.

boge, and mastic, and were able to get particles having diameters as small as about $2\text{ m}\mu$. They determined experimentally the sedimentation equilibrium, osmotic pressure, diffusion, and Avogadro's number, and found that laws based on the kinetic theory did hold for these colloidal solutions. Since then a tremendous amount of experimentation has been done with such colloidal solutions. Despite the fact that these artificially produced colloids have been found to be polydisperse (44) and that certain minor discrepancies have been noticed (17), it is still generally acknowledged that the laws governing ideal gases tend to apply to most colloidal solutions, that is, solutions of particles having diameters ranging upwards from about $2\text{ m}\mu$. Nevertheless, Graham's ideas have persisted and there has been a tendency to segregate solutions into colloidal solutions and "true" solutions. The abundance of substances such as gold, silver, mastic, etc. which could be obtained in the form of small particles and the relative lack of macromolecules probably fostered this situation.

The rise of protein chemistry, as evidenced by the work of Sorenson (34) and Osborne (29), the chemical studies of Loeb (22), Northrop's studies on enzymes (26) and other proteins (27), the solubility studies of Cohn (9), and especially the ultracentrifugal studies of Svedberg (45, 14), has not only supplied the colloid chemist with a great group of macromolecules, but has forced down practically all barriers between colloidal solutions and "true" solutions. This group of proteins includes those having sedimentation constants² of from 2 to 130, corresponding to molecular weights of from about 18,000 to 10,000,000, and on the basis of spherical molecules to diameters of from about 1 to $25\text{ m}\mu$. The work of the investigators just mentioned has demonstrated that, although the molecules of these proteins are of colloidal size, they nevertheless possess many of the properties of ordinary molecules and their solutions may be considered "true" solutions. The protein molecules already described have thus not only bridged the gap between ordinary molecules and colloidal particles, but with respect to size have actually trespassed into the realm of colloidal gold and silver particles. However, the artificially produced colloids have remained as the sole representatives of particle sizes ranging upward from about $25\text{ m}\mu$, for the hemocyanin protein molecules with diameters ranging from about 8 to $25\text{ m}\mu$ have been the largest hitherto reported (14). The purpose of the present paper is to describe the isolation and properties of a new group of macromolecules, the virus proteins (35), the molecules of which are larger than those of any protein previously described. The smaller virus proteins have sedimentation constants of the same order as those of the largest hemocyanins and the largest virus proteins may prove to have sedimentation constants of the order of a few thousand. Despite their tremendous size, the virus pro-

² The sedimentation constants are expressed in units of 10^{-13} .

conclusion that they either are or are not protein molecules. In view of the results with some of the smaller viruses, there should be no objection to using, as a working hypothesis, the idea that the largest viruses are also macromolecules.

The question of identity of protein with virus activity

Although the question as to whether or not the virus activity is a specific property of these macromolecules is probably of greatest interest to pathologists and bacteriologists, it is deemed of sufficient interest to colloid chemists to warrant a brief review at this place of some of the experimental data. Since tobacco mosaic virus protein has been subjected to the most extensive investigation, most of the data to be presented will refer to this virus protein (see reference 37 for recent bibliography).



FIG. 1. Crystalline tobacco mosaic virus protein. $\times 675$. (Photograph by J. A. Carlile)

Figure 1 is a reproduction of some of the crystals of tobacco mosaic virus protein which were prepared by Dr. Loring. These crystals are actually quite small, for they are only about 0.02 to 0.03 mm. in length. It is possible to vary their size by a factor of about 10 by changing the conditions of crystallization. It seems likely that their form is different from that of the material reported by Best (4), for vigorous shaking does not cause these crystals to break up into invisible units. They are true crystals, since they are doubly refractive and give a regular crystalline pattern on x-ray analysis (53). A typical elementary analysis is given in table 1. A typical dilution curve showing the virus activity of the protein as tested on *Phaseolus vulgaris* plants is given in figure 2. This dilution series was prepared by mixing 1 cc. of a solution containing 10 mg. of virus protein per cubic centimeter with 9 cc. of 0.1 M phosphate

buffer at pH 7, then mixing 1 cc. of this solution with 9 cc. of phosphate buffer, etc. The pipets and glassware used were chemically clean and had not been specially treated. The virus activity of the protein may be determined by rubbing, by means of a small bandage gauze pad, a solution containing a known amount of the protein over the upper surfaces of the leaves of certain plants. About forty-eight hours later there will appear on the leaves many spots or lesions if there was much virus protein in the solution and but a few spots or lesions if there was but little virus pro-

TABLE 1

Elementary analysis and optical activity of crystalline tobacco mosaic virus protein

	C	H	N (DUMAS)	P	ASH
Per cent of dry weight.....	50.74	7.56	16.56	0.51	0.53
Optical activity $[\alpha]_D^{20}$ per milligram of nitrogen.....	<div style="display: flex; justify-content: space-between; align-items: center;"> 0.42 </div> <div style="display: flex; justify-content: space-between; align-items: center;"> 0.44 </div>				

Samples in dilute sodium hydroxide at pH 11.2 ± 0.1

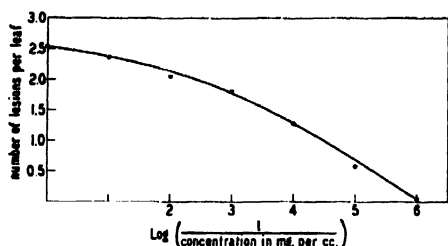


FIG. 2

FIG. 2. Dilution curve of tobacco mosaic virus protein in 0.1 M phosphate buffer at pH 7

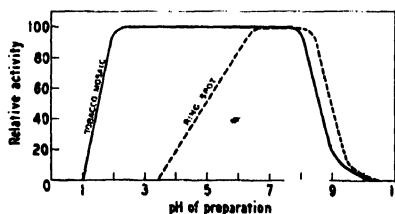


FIG. 3

FIG. 3. The activity, as measured by the lesions obtained with test solutions expressed as a percentage of those obtained with controls, of tobacco mosaic virus protein and of tobacco ring spot virus protein after one day at various pH values and readjustment to pH 7.

tein in the solution. Thus the number of lesions obtained serves as a rough index of the amount of virus. The activity of one solution may be compared with that of another by applying one to the right or left halves of all of the leaves and the other to the remaining halves of all the leaves. This method suitably standardized is used to measure virus concentration, and it is sufficiently accurate so that differences in virus concentration greater than about 10 per cent may be detected without difficulty using only about forty to fifty leaves (23).

In table 2 data from recent work (24) are reproduced in which the ac-

teins have many of the properties of ordinary molecules. Although it is possible that further work may reveal such confusing dissociation phenomena as that exhibited by hemoglobin (42) and by some of the hemo-cyanins (14), all of the data available at present indicate that the virus proteins fulfill the accepted chemical definition of a molecule as the smallest weight which cannot be subdivided without a complete change in the properties. This new group of macromolecules bridges the last gap between particles visible under the microscope and molecules, hence the colloid chemist now has at his disposal molecules ranging in diameter from that of the very small hydrogen molecule up to that of the largest virus protein, which may prove to be of the order of 200 m μ .

THE NATURE OF VIRUSES (8, 31)

Viruses are submicroscopic infectious entities which are capable of causing disease in man, animals, plants, insects, and bacteria. Such diseases as the various types of encephalitis, poliomyelitis, measles, yellow fever, certain types of tumorous growths, the common cold, rabies, dog distemper, foot-and-mouth disease, and the several mosaic and yellows diseases of plants are considered to belong in the group of diseases caused by viruses. In the past, viruses have been characterized by their invisibility, by their ability to pass filters capable of holding back ordinary bacteria, and by their inability to multiply in the absence of living cells. However, even these general characteristics have not been completely acceptable, for there have been reports that some viruses have been seen, others held back by filters, and still others cultivated in the absence of living cells. The confused state of knowledge concerning even the simple basic properties of viruses has led to an even greater confusion regarding the nature of these agents. They have been regarded variously as protozoa, as invisible forms of ordinary bacteria, as a new kind of invisible living organism, as unusual products of cellular metabolism, as enzymes, and as different kinds of inanimate chemical substances. However, because viruses may multiply or reproduce, because they are specific in that certain ones occur or cause disease only in certain hosts, because they may change or mutate and adapt themselves to new conditions, and because of the lasting immunity which follows most virus diseases, the majority of the workers in the virus field have chosen to regard viruses as invisible living organisms. It is obvious that the arguments for the living nature of viruses are very strong, for the properties just enumerated are characteristic of living things. However, certain other properties, such as their small size and their inability to grow on lifeless media, suggested that they might differ somewhat, and they have been placed, therefore, in a group apart from ordinary living organisms and have been called viruses.

EXPERIMENTAL

The isolation of virus proteins

The virus selected for initial study was tobacco mosaic, the first of all viruses to be discovered (16). It was selected because of its unusual stability, its high infectivity, and its ready availability. After several years of preliminary experimentation, much of which was based on the earlier work of Vinson (48) and others, it was found possible to isolate from mosaic-diseased Turkish tobacco plants a crystalline protein (35, 37). This protein was unusual in that its molecules were found to possess the properties of the virus and to be considerably larger than those of any other known protein, for the molecular weight was found to be 17,000-000 (13). This work was immediately extended to include the study of other viruses. Crystalline tobacco mosaic virus protein was first isolated early in 1935 by chemical means. The same methods were successfully used in the isolation of several different strains of tobacco mosaic virus, but difficulty was encountered when they were applied to certain of the less stable viruses. In the meantime, it had been found (54) that crystalline tobacco mosaic virus protein could be readily obtained by centrifuging the extracts of diseased plants by means of the newly developed air-driven quantity centrifuge (1, 7, 50, 51). The very rapid and effective centrifugal method was used, therefore, for the less stable viruses and found to be very successful (41). Turkish tobacco plants diseased with latent mosaic of potato (X-virus) were examined and a high molecular weight crystalline protein with a sedimentation constant of about 113 and possessing the properties of this virus was isolated. From Turkish tobacco plants diseased with ring spot virus a crystalline protein having a sedimentation constant of about 115 was isolated. A protein having a sedimentation constant of about 180 was isolated from plants diseased with severe etch virus. This study has recently been extended to include viruses affecting animals, and Beard and Wyckoff (3), using the air-driven quantity centrifuge, were able to isolate from virus-induced rabbit papillomas a protein having a sedimentation constant of about 250 and having the properties of the virus. Bacteriophage may be regarded as a virus disease of bacteria, and in this connection it is interesting to note that Northrop (28) has isolated a high molecular weight protein from bacteriophage-infected staphylococcus cultures, and Schlesinger (32) has obtained a protein-containing material having a particle size of about 100 m μ from coli-phage infected colon bacillus cultures. The largest of the viruses, such as those causing the pock diseases, are thought to be about 200 m μ in diameter (6, 12). Although, with the sole exception of size, these large viruses appear to be similar to the small viruses, insufficient experimental evidence is available at present to justify the definite

tivity of once-crystallized protein is compared with that of fifteen-times-crystallized protein. It may be seen that in experiment No. 1, test No. 1, a solution containing 10^{-5} g. of once-crystallized protein per cubic centimeter, on inoculation to the halves of forty-two bean leaves, gave an average of 66.6 lesions per half-leaf, whereas a solution containing 10^{-5} g. of

TABLE 2

Relative infectivity of tobacco mosaic virus protein after one crystallization and after fifteen crystallizations

EXPERIMENT	TEST	PREPARATION	CONCENTRATION IN GRAMS OF PROTEIN PER CC.	
			10^{-5}	5×10^{-6}
1†	1	Crystallized once	66.6*	43.3
		Crystallized fifteen times	68.4	49.0
		Number of half-leaves	42	42
		M.D./S.D.†	0.44	1.4
	2	Crystallized once	38.6	34.5
		Crystallized fifteen times	35.5	32.9
		Number of half-leaves	44	44
		M.D./S.D.	1.05	0.47
2‡	1	Crystallized once	79.8	38.4
		Crystallized fifteen times	72.5	47.0
		Number of half-leaves	44	44
		M.D./S.D.	1.59	2.57
	2	Crystallized once	51.1	42.4
		Crystallized fifteen times	55.3	41.9
		Number of half-leaves	34	36
		M.D./S.D.	0.98	0.12

* Numbers opposite a particular preparation represent the average number of necrotic lesions per half-leaf obtained on *Phaseolus vulgaris* on inoculation with the designated preparation and concentration. A given preparation was administered to the right halves of half of the leaves and to the left halves of the remaining leaves in each test.

† To show a significant difference between the mean number of lesions in any one experiment, the ratio of the difference of the mean (M.D.) to the standard deviation of the difference (S.D.) should be not less than 2.1.

‡ In experiment No. 1, 30 per cent, and in No. 2, 81 per cent of the original amount of virus protein was lost in the mother liquor during recrystallization.

fifteen-times-crystallized protein per cubic centimeter, on inoculation to the other halves of the same forty-two bean leaves, gave an average of 68.4 lesions per half-leaf. The odds are less than 20 to 1 that the activity of these two solutions is different, hence it is concluded that there is no difference in their virus activity. Examination of the results reveals the

fact that the tobacco mosaic virus protein may be crystallized fifteen successive times without changing its virus activity, and that it may be fractionally crystallized so that only 19 per cent of the original amount of protein remains without any change in the specific virus activity. The crystalline protein obtained from many different lots of plants diseased with the same virus strain has the same chemical composition, isoelectric point, optical rotation, x-ray diffraction pattern, sedimentation constant, and biological activity. The absorption spectrum of the virus protein was found to agree essentially with the destruction spectrum of the virus activity (21). The same protein was isolated from many different species of plants diseased with the same virus strain, whereas somewhat similar although different proteins were isolated from the same species of plant diseased with different strains of a given virus and markedly different proteins were isolated from the same species of plant diseased with different viruses. For example, the same protein was isolated from Turkish and Burley tobacco, tomato, phlox, and spinach plants diseased with ordinary tobacco mosaic virus, whereas four somewhat similar proteins differing in certain respects were isolated from four groups of Turkish tobacco plants diseased with four different strains of tobacco mosaic virus, and three completely different proteins were isolated from three groups of Turkish tobacco plants diseased respectively with latent mosaic, tobacco ring spot, and severe etch viruses. The different virus proteins may be characterized by their sedimentation constants, pH stability range, solubility, isoelectric point, heat coagulation point, x-ray diffraction pattern, immunological reactions, and biological activity. For example, the sera of animals injected with a solution of tobacco mosaic virus protein give a precipitin test when mixed with solutions containing but 10^{-6} g. per cubic centimeter of tobacco mosaic virus protein or protein of closely related strains and fail to give a precipitate when mixed with solutions of latent mosaic or ring spot virus proteins. Likewise, antisera to ring spot virus protein fail to react with tobacco mosaic or latent mosaic virus protein. Treatment of tobacco mosaic virus protein with hydrogen peroxide, formaldehyde, nitrous acid, or ultra-violet light produces inactive native proteins that, although slightly altered chemically, retain certain chemical and serological properties characteristic of the virus protein (36). The sera of animals injected with a solution of inactive protein have a neutralizing effect *in vitro* on virus activity not possessed by normal sera. This point may prove of importance, for it is a demonstration that a virus can be inactivated without seriously changing its immunological properties.

The x-ray diffraction patterns of tobacco mosaic, latent mosaic, and ring spot virus proteins have been determined and found to be different. The pH stability ranges of the activity of tobacco mosaic virus protein

(5, 38) and of tobacco ring spot virus protein (40) have been determined and are given in figure 3. Ring spot and latent mosaic virus proteins are much less stable towards acid and slightly more stable towards alkali than tobacco mosaic virus protein. The virus proteins lose their virus activity when they are denatured by acid, by alkali, or by heating. Tobacco mosaic virus protein coagulates on heating to about 75°C., whereas ring spot virus protein coagulates at 64°C. The isoelectric point of the former is at pH 3.5 and of the latter at pH 4.7. A marked Tyndall cone is shown when a beam of light is passed through solutions of virus proteins. The amounts of the different virus proteins occurring in the same species of host have been found to vary widely. In Turkish tobacco plants tobacco mosaic virus protein reaches a concentration of from 2 to 4 mg. per cubic centimeter of extract, latent mosaic virus protein a concentration of about 0.2 mg. per cubic centimeter of extract, and ring spot virus protein a concentration of about 0.02 mg. per cubic centimeter of extract. In accordance with this, tobacco mosaic virus protein was found to be about 500 times, latent mosaic virus protein about 5000 times, and ring spot virus protein about 50,000 times more active than the starting material. Beard and Wyckoff (3) were able to isolate about 1 part per 4000 of the rabbit papilloma tissue in the form of a homogeneous protein having a sedimentation constant of about 250. They found the activity of the virus protein to be several thousand times that of the starting material. The papilloma virus protein was found to coagulate on heating to 66-67°C., and Shope (33) has reported that the virus activity of papilloma extracts begins to diminish at 67°C. and is completely destroyed at 70°C.

The fact that the virus proteins behave as macromolecules makes possible a new and different method of approaching the question concerning the identity of activity and protein, for their tremendous size makes it possible to centrifuge the protein molecules from solution under a variety of conditions. If the virus activity is a specific property of the high molecular weight protein, then, following centrifugation of different amounts of protein from solutions at different hydrogen-ion concentrations or from solutions containing other proteins, the virus activity of the upper portions of the centrifuged solutions should be diminished and be proportional to the amount of high molecular weight virus protein that they contain. Such experiments have been carried out with tobacco mosaic virus protein, and in every instance the virus activity of the various samples was found to be proportional to the amount of high molecular weight virus protein present (39). Representative results obtained on centrifuging tobacco mosaic virus protein on either side of the isoelectric point are given in table 3. This protein is insoluble at the isoelectric point and when centrifuged gives a protein-free and inactive supernatant.

Sedimentation constants

The very high molecular weights of the virus proteins make it quite difficult to determine molecular weights by ordinary methods or even by means of diffusion or osmotic pressure measurements. For example, in the case of tobacco mosaic virus protein, although it was possible by means of the diffusion and osmotic pressure to determine that the molec-

TABLE 3

*Correlation of virus activity and protein on centrifugation of tobacco mosaic virus protein at pH 2.4, 6.7, and 9.4**

pH DURING CENTRIFUGATION	PROTEIN CONCENTRATION AFTER CENTRIFUGATION IN MG. PER CC.	PORTION OF CENTRIFUGED SAMPLE USED	PROTEIN CONCENTRATION USED FOR TESTS IN GRAMS PER CC.	
			10 ⁻⁴	10 ⁻³
2.4	1.2	Upper portion	57.9†	25.3
	28.3	Lower portion	62.1	30.4
		Number of half-leaves	52	52
		M.D./S.D.‡	0.96	2.34
6.7	1.2	Upper portion	145.0	74.8
	16.8	Lower portion	161.2	82.8
		Number of half-leaves	56	56
		M.D./S.D.	2.02	1.89
9.4	2.1	Upper portion	128.6	67.6
	16.7	Lower portion	142.1	74.5
		Number of half-leaves	56	56
		M.D./S.D.	2.09	1.91

* Tests following dilution of lower portions to same protein concentration as in the corresponding upper portions of centrifuged samples. All dilutions were made with 0.1 M phosphate buffer at pH 7. *Phaseolus vulgaris* was used as the test plant.

† Numbers opposite a given preparation represent the average number of lesions per half-leaf obtained on inoculation with the designated preparation and concentration. A given preparation was administered to the right halves of half of the leaves and to the left halves of the remaining leaves in each test.

‡ To show a significant difference between the mean number of lesions in any one experiment, the ratio of the difference of the mean (M.D.) to the standard deviation of the difference (S.D.) should be not less than 2.1.

ular weight was of the order of several million (35), it was found impossible to secure satisfactory duplication of the results. The ultracentrifugal method for the determination of molecular weights (45), however, is especially suited for such macromolecules. Dr. Svedberg was supplied with a sample of crystalline tobacco mosaic virus protein, and the first sedimentation constant determinations of a virus protein were made in

his laboratory at Upsala (13). This sample of virus protein proved to have a sedimentation constant of about 200 and to be inhomogeneous with respect to molecular weight. The protein was found to be completely homogeneous with respect to isoelectric point. At pH 9.8 the protein was found to have formed two components having sedimentation constants of 185 and 125, respectively, and at pH 11.7 it was found to have been split into low molecular weight components having constants of 8.1 and 3.8, respectively. Since tobacco ring spot virus protein becomes largely inactivated on standing at room temperature for twenty-four hours, and since even the supposedly very stable tobacco mosaic virus protein has been found to change somewhat on merely standing for several days, it has been found preferable to carry out the determinations as soon as possible after the isolation of the protein. The recent ultracentrifugal studies have been performed, therefore, by Dr. Wyckoff at the Princeton laboratories of The Rockefeller Institute. The previously determined sedimentation constants for tobacco mosaic virus protein have been confirmed (54), virus protein completely homogeneous with respect to molecular weight has been obtained, and the work has been extended to include a study of the pH stability range of the different virus proteins (52).

Shape of molecule

Svedberg (13) found that the molecular weight of the tobacco mosaic virus protein obtained from sedimentation equilibrium determinations was of the same order of magnitude as that calculated from the sedimentation constant on the assumption of a dissymmetry constant $f/f_0 = 1.3$, a value found for other high molecular weight proteins. This result, although somewhat uncertain, owing to the low diffusion of the protein, nevertheless indicates that the molecules depart somewhat from a spherical shape. Takahashi (46) in 1933 noticed that the clarified juice from mosaic-diseased Turkish tobacco plants exhibited double refraction of flow. Solutions of crystalline tobacco mosaic virus protein have recently been examined and have also been found to show double refraction of flow (47); it was concluded that the virus protein is composed of rod-shaped particles. Other workers (2), on the basis of x-ray data, have also concluded that the molecules of this virus are rod-shaped and have a minimum length not less than ten times the width.

If the dissymmetry is of an extreme nature so that the molecules more nearly resemble threads than elongated ellipsoids, it seems likely that their solutions should be unusually viscous. For example, the viscosity of muscle globulin, which is supposed to be comprised of rod-shaped molecules, is quite high. The relative viscosities of solutions of tobacco

mosaic virus protein, of the high molecular weight *Limulus polyphemus* hemocyanin,³ and of egg albumin³ have been determined and compared with that of muscle globulin as recorded by Edsall (10) and with that of gelatin as determined by Kunitz (18). It may be seen from the results, which are given in figure 4, that the viscosity of the virus protein is considerably smaller than that of muscle globulin and lies between that of

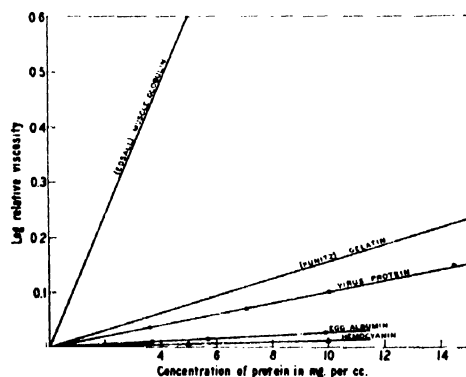


FIG. 4

FIG. 4. Viscosity-concentration curves for tobacco mosaic virus protein at 25.6°C. $\pm 0.2^\circ$ in 0.1 M phosphate buffer at pH 7 and for other proteins.

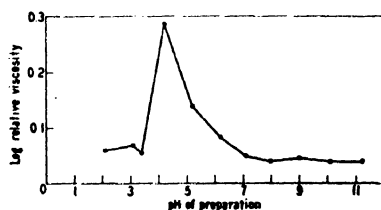


FIG. 5

FIG. 5. The viscosity at different hydrogen-ion concentrations of a solution containing 5.5 mg. of tobacco mosaic virus protein per cubic centimeter in 0.075 M buffer.

TABLE 4

Hydration of tobacco mosaic virus protein as determined from viscosity in 0.1 M phosphate buffer at pH 7 and 25.6°C. $\pm 0.2^\circ$

CONCENTRATION OF PROTEIN IN MG. PER CC.	RELATIVE VISCOSITY	CALCULATED VOLUME OF HYDRATED PROTEIN IN CC. PER 100 CC. OF SOLUTION	VOLUME IN CC. OF HYDRATED PROTEIN PER GRAM OF DRY PROTEIN	VOLUME IN CC. OF WATER OF HYDRATION PER GRAM OF DRY PROTEIN
1.0	1.025	0.6	6.0	5.2
3.6	1.094	2.1	5.8	5.0
10.0	1.270	5.3	5.3	4.5
14.5	1.417	7.6	5.3	4.5
28.7	2.140	15.9	5.5	4.7
47.7	3.630	25.2	5.3	4.5

gelatin and of egg albumin and hemocyanin. This may be regarded as indicating that the dissymmetry is not of an extreme nature. The viscosity of the virus protein at various hydrogen-ion concentrations is given in figure 5. It may be seen that the relative viscosity becomes greater

³ The writer is indebted to Dr. C. V. Seastone for this sample of hemocyanin and to Dr. M. Kunitz for a supply of crystalline egg albumin.

as the isoelectric point is approached from the alkaline side and then falls off rapidly as the protein crystallizes from solution. The solution of the protein at pH 2 has about the same viscosity as have solutions at hydrogen-ion concentrations between pH 7 and 11. The specific volume of the protein was determined pycnometrically using toluene and butyl alcohol; the value found was 0.77. This is somewhat higher than that previously reported (13). The water of hydration per gram of dry protein has been calculated from the density and from the viscosity data, using Kunitz's empirical equation (18); the results are given in table 4. The value obtained is considerably larger than that found for hemoglobin and trypsin (19) and is of the same order as that of gelatin (18). As a whole, the ultracentrifugal results, the orientation phenomenon, and the x-ray and viscosity data may be considered to be in harmony with the idea that the length of the tobacco mosaic virus protein molecule may be of the order of ten times the width. Similar data are not now available with respect to other virus proteins. However, the obvious orientation phenomenon has not been observed in the case of the tobacco ring spot virus proteins. It is possible, therefore, that the proteins of tobacco mosaic virus and its strains may differ somewhat from those of other viruses with respect to shape.

THEORETICAL CONSIDERATIONS

The virus proteins not only bridge the gap between molecules and artificially prepared colloidal particles, but they also bridge the gap between molecules and living organisms. The smaller virus proteins (latent mosaic virus protein, $S_{20} = 113$) are of the same order of size as the largest hemocyanin molecules (*Busycon canaliculatum* hemocyanin, $S_{20} = 130$ (14)), whereas the largest viruses (vaccine virus, diameter = about 175 m μ (12)) are of the same order of size as admittedly living organisms (bovine pleuro-pneumonia, diameter = about 150 m μ (12); sewage organism, diameter = about 200 m μ (20)). Shall the virus proteins be classified as molecules or as living organisms? Since they have been shown to possess the ordinary chemical properties which are characteristic of molecules and to react as molecules, the chemist would be inclined to regard them as molecules. However, in addition to the chemical properties which they possess as molecules, they also possess virus activity. In a test tube or when applied to a non-susceptible host, virus proteins appear as inanimate matter, devoid of special activity. Yet, when a few molecules of a virus protein are administered to the living cells of a susceptible host, they immediately bring about the production of millions of molecules of the same kind. In living cells and only in the living cells of a susceptible host have they been found to reproduce or multiply, and this production of new virus protein results in what we call disease. Because

of this reproductive power, they have been called autocatalysts (35). Although this is technically incorrect in that the reaction is very probably not that of true autocatalysis, the term was used because the net result is somewhat similar to that of an autocatalytic reaction. However, the mechanism by means of which a molecule in a specific living cell is able to cause the production of identical or similar molecules is unknown. It may be similar to the mechanism which the geneticists postulate for the production of genes (25). The virus protein molecule may be able to cause smaller molecules already present in the cell, or smaller molecules produced by the cell as a result of the presence of the virus molecule, to organize and combine to form a new virus molecule. It is an amazing fact that living cells are able at a moment's notice to produce millions of molecules of any one of a number of different virus proteins depending upon the exact molecule introduced, and yet be entirely unaffected by still other virus proteins. Another amazing phenomenon is that, although a cell exhibits a remarkable tendency to produce only exact duplicates of the virus protein molecule introduced, there is a slight but distinct tendency to produce a few slightly differing molecules. The reproduction of such slightly different molecules and their subsequent separation and isolation give rise to new strains of the virus. This phenomenon, in which the virus protein becomes changed and gives rise to a new strain causing a new disease, has been called mutation.

Because viruses may reproduce and mutate, and because of their specificity and the lasting immunity they usually induce, pathologists and bacteriologists have for years regarded them as submicroscopic living organisms. Since the virus protein molecules possess such properties, many workers today choose to regard these macromolecules as living organisms. It is obvious that as molecules they possess properties which differ somewhat from the ordinary properties of molecules and that as organisms they possess properties which differ somewhat from the ordinary properties of organisms. In this paper the properties of viruses as macromolecules have been stressed. This has been done because the advances in virus research which have been made in the past few years have resulted largely from the consideration of viruses as chemical entities and the virus proteins as macromolecules. Further attempts to classify viruses more exactly as either molecules or as organisms should await more experimental data.

SUMMARY

Colloid chemistry originally evolved from knowledge of particles rather than of molecules, and for years colloidal solutions of particles consisting of aggregates of molecules were supposed to differ from solutions of mole-

cules. It was shown on theoretical grounds and later proven experimentally that the laws based on the kinetic theory applied to colloidal solutions as well as to solutions of molecules. The tendency to segregate colloidal solutions remained until several workers demonstrated that solutions of proteins having molecular weights ranging up to about ten million were solutions of molecules, despite the fact that they exhibited many of the properties of colloidal solutions. The discovery that many of the viruses, which as a group range in size from about 5 to 200 $m\mu$, are protein molecules thus makes available a new group of macromolecules. The virus protein of tobacco mosaic, an infectious disease of certain plants, has been subjected to extensive investigation. It has been obtained in crystalline form and has been found to be homogeneous with respect to size and isoelectric point and under specified conditions to possess constant properties such as composition, isoelectric point, optical rotation, x-ray diffraction pattern, sedimentation constant, absorption spectrum, immunological reactions, solubility, pH stability range, heat coagulation point, and biological activity. Despite its tremendous size, tobacco mosaic virus protein has many of the ordinary properties of molecules. In addition, however, it possesses virus properties which include the ability to reproduce and to mutate, specificity of action with respect to host, and the ability to induce immunity. Several virus proteins, some from other plant diseases and some from animal and bacterial diseases, some larger and some smaller than tobacco mosaic virus protein, have been isolated and are now under investigation in various laboratories. The virus proteins thus represent a new group of macromolecules which are considerably larger than those of any group of proteins hitherto described. Because of this tremendous size, the air-driven quantity centrifuge and the ultracentrifuge are peculiarly adapted to the isolation and study of the virus proteins. Since the virus proteins possess virus activity and certain properties characteristic of organisms, as well as the properties of molecules, any attempt at this time to classify them definitely as molecules or as organisms should be one solely of convenience. However, their characterization as molecules is providing a new experimental approach to the general problem of the nature of viruses.

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ELECTROKINETIC ASPECTS OF SURFACE CHEMISTRY. I

THE ELECTROPHORESIS OF ADSORBED EGG ALBUMIN¹

LAURENCE S. MOYER

Department of Botany, University of Minnesota, Minneapolis, and The Biological Laboratory, Cold Spring Harbor, Long Island, New York

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The properties of protein surfaces have become of increasing importance, especially in biological systems. In view of their complexity, it seems desirable to examine in some detail the characteristics of adsorbed surface films of proteins and of protein particles, and the influence of the adsorption process on the electrical properties of the surface. The data extant are difficult to interpret because of differences in method. Thus, the small discrepancy noted between the electric mobility of dissolved egg albumin investigated with the moving-boundary method of Tiselius (31) and that of adsorbed egg albumin studied by Abramson (4) and Smith (26, 27) emphasizes the need for a special investigation of this protein surface in an attempt to determine the cause of the differences observed. Since the work of Ramsden (23), it has been realized that egg albumin denatures when at an air-water interface. In any investigation of this character one must distinguish carefully between surfaces of normal and surface-denatured egg albumin. Furthermore, the possibility of poly-molecular films consisting of a surface-denatured layer coated with partially denatured or oriented layers, together with the possible effect of the underlying surface, must be kept in mind.

Tiselius, using egg albumin crystallized from solutions of ammonium sulfate by the method of Sørensen (29) and electro-dialyzed, concluded that the isoelectric point lies at pH 4.55 in *M*/50 sodium acetate buffer at 20°C. More recently Annetts (6), working in the same laboratory, has reported a single mobility value at pH 5.0 which agrees closely with Tiselius' curve. The concentration used by Annetts was 2 per cent albumin, whereas Tiselius usually used about 0.3 per cent.

A number of "inert" surfaces have been shown by Abramson and others (2, 4, 21) to be identical in behavior in the electric field when coated with any one of several proteins if the concentration is high enough to insure a complete film. It has also been shown by Abramson (2) that the mo-

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bility curve of purified egg albumin (Sørensen) adsorbed on quartz is nearly parallel but not identical with that of dissolved albumin. The position of the isoelectric point was found to be dependent on the ionic strength, shifting to lower pH values as the sodium acetate concentration is increased (3). The influence of ionic strength on the isoelectric point has been specially investigated by Smith (26). She found that the isoelectric point of quartz and collodion particles suspended in egg albumin is at pH 4.82-4.83 in $M/50$ sodium acetate buffer. In a later paper, the same author (27) has demonstrated that the nature of the crystallizing salt, ammonium sulfate (Sørensen) or sodium sulfate (Kekwick and Cannan (13)), produces very little or no effect on the isoelectric point (< 0.01 pH at $M/50$ acetate). The pH of the isoelectric point in acetates was found to be linearly related to the ionic strength, being increased by divalent and trivalent cations and decreased by univalent cations. Of all these salts, lithium acetate had least effect. Extrapolation to zero ionic strength for each cation gave a common isoelectric point of pH 4.86 ± 0.02 , a value in close agreement with the isoionic point in the absence of salt at pH 4.88 deduced by Sørensen, Linderstrøm-Lang, and Lund (30). In their excellent work on the titration curve, Kekwick and Cannan (13) likewise found no significant difference in titration curve between samples of egg albumin prepared by the two methods mentioned.

These different values for the isoelectric point can scarcely be ascribed to differences in the electrophoretic techniques employed by the investigators cited, for it has been shown that measurements in U-tubes agree completely with those made in vertical and horizontal microelectrophoresis cells (5). In any case, the position of the isoelectric point should be nearly independent of the construction and calibration of the electrophoresis instrument, since no motion of liquid or particles occurs in a cell with the surface of both the particles and wall at the isoelectric pH (4, 21).²

It is our purpose in this communication to present careful measurements of electric mobilities of highly purified normal and surface-denatured egg albumin adsorbed on a variety of surfaces, in an endeavor to throw light on the nature of adsorbed protein films, which, it is now realized, are of so much importance in biology and medicine (4, 5, 17, 20).

MATERIALS AND METHODS

Electrophoretic measurements

Measurements of electrophoresis were made with two horizontal Abramson microelectrophoresis instruments (4), using methods described in detail elsewhere (19). Human erythrocytes were used to check the

² Measurements of the isoelectric point in the center of the cell are valid only if $R = 1$.

calibration of these instruments, for it has been shown that the surface of the red blood cell is extremely constant in behavior (4, 5). Both instruments gave a value of 1.30μ per second for the electric mobility of red cells in $M/15$ phosphate buffer at pH 7.4; this is within 1 per cent of the best data available (4).

It is not generally realized that for systems where the surface of the wall of the chamber and the surface of the particle are identical (i.e., the ratio R of electroösmosis to electrophoresis is 1.0) the theories of Smoluchowski and Komagata permit measurements to be made at the middle of the cell where the velocity gradient is zero. This practice is of advantage for suspensions near the isoelectric point, where it is desirable to time particles moving with as great a velocity as possible.

When the cell is wide and the equation of Smoluchowski applies (4),

$$V = 2/3 V_{0.5} \quad (1)$$

where V is the true velocity and $V_{0.5}$ the velocity at the center of the cell.

In general, the parabola,

$$v_{\text{obs.}} = b(x - x^2) + c \quad (2)$$

(where x is the fraction of the total depth at which the observed velocity $V_{\text{obs.}}$ is obtained; b and c are constants) can be used to describe the $V_{\text{obs.}}$ -depth curve (21). Komagata (14) has presented measurements in cells whose ratio of width to depth, k , is as small as 6, yet even in these cases equation 2 can be fitted to his data. Here, let $c = 0$ (since electroösmosis = electrophoresis) and let the true mobility be that obtained at the depth $x = a$. Then,

$$V = 4V_{0.5} (a - a^2) \quad (3)$$

Transforming Komagata's equation for flat closed cells into terms of fractional depth measured from the top of the cell, we have

$$a = \frac{1}{2} \pm \sqrt{\frac{1}{12} + \frac{32}{\pi^2 k}} \quad (4)$$

On substitution of this expression in equation 3, it is found that

$$\left(\frac{2}{3} - \frac{128}{\pi^2 k}\right) V_{0.5} \quad (5)$$

Table 1 shows a comparison between experiment and theory. Komagata's data were reduced to $c = 0$ by subtracting the intercept on the $V_{\text{obs.}}$ axis from $V_{\text{obs.}}$. The observed values for V were interpolated from smooth curves. The cells used in our work had values of $k > 20$.

Smith and Lisse (28) have recently described a new double-tube cylindrical cell in which measurements are made at the axis of the smaller tube where the velocity gradient is zero. It will be seen that the flat cell also possesses these advantages when $R = 1.0$.

In the present experiments, particles were measured at the usual stationary levels (equation 4) except in certain cases when it was clear that $R = 1.0$ (21) and the particles were moving too slowly to be easily timed at the 0.2 and 0.8 levels.

Protein preparations

Five distinct preparations of egg albumin were prepared from fresh hen's eggs (< 1 day old) by crystallizing four times from sodium sulfate by the method of Kekwick and Cannan (13). Two preparations were crystallized at 25°C ., the rest at 32°C .. One preparation was dried while in the crystalline state (13). The crystallizing salt was added very cau-

TABLE 1

Comparison of velocities calculated from measurements at the center of the cell with observed at the stationary level in cases when $R = 1.0$

OBSERVER		V (OBSERVED)	V (CALCULATED FROM EQUATION 5)	V (CALCULATED FROM EQUATION 1)	ERROR FROM USE OF EQUATION 1
					<i>per cent</i>
Komagata.	6.0	5.3	5.4	6.3	14
Komagata.....	12.0	6.9	6.9	7.3	6
Moyer.....	20.6	1.29	1.28	1.34	5

tiously, as directed, until microscopic examination revealed well-formed albumin crystals. Precipitates formed when the salt was added too rapidly adsorbed impurities and made purification difficult. The resultant preparations were dialyzed until the specific conductance was of the order of 1×10^{-4} mho. They were kept covered with a mixture of washed mineral oil and toluene and stored in a refrigerator. One preparation, which showed a trace of opalescence, gave abnormal values (see below); on filtration through No. 40 Whatman filter paper, values were identical with data secured from unfiltered preparations which had clarified by slow settling. No differences were ever found between preparations if suitable care was taken. All preparations were absolutely water-clear. Preliminary preparations with only traces of color gave anomalous results. Concentrations were determined by drying a weighed sample at 110°C .

Schulz and Zsigmondy (25) have proposed the use of the gold number in testing the purity of egg albumin. A high gold number indicates purity,

i.e., a low protective action. They state that pure crystalline egg albumin should give gold numbers between 2 and 8; traces of ovomucoids or other proteins reduce these values to 0.03-0.05. Gold numbers were obtained with three of our preparations; each was greater than 7. As a further check on the purity, a quantitative estimation of the amount of heat-denaturable albumin in one preparation showed that it was 100 per cent denaturable (within 0.5 per cent).

Buffer mixtures

Unless otherwise mentioned, mobility determinations were carried out in *M*/50 sodium acetate buffers of constant ionic strength. These were prepared from standard acid and alkali. Hydrogen-ion activity was usually measured by the quinhydrone electrode and checked by the Clark rocking hydrogen electrode over the range of pH investigated. In one series the glass electrode was used.³ Values of pH are referred to the pH of an equimolar mixture of *M*/100 sodium acetate-acetic acid, $pK' = 4.70$. This mixture gives values in agreement with *N*/10 hydrochloric acid, pH 1.08, with the added advantage of less variability in liquid junction potential.⁴ No corrections were needed because of the low protein and salt concentrations.

Preparation of particles

Quartz particles were carefully cleaned and fractionally sedimented by the method of Abramson (1). Pyrex glass particles were prepared by grinding clean Pyrex glass in a mortar and sifting to get particles passing 300 mesh. Decolorizing carbon and mineral oil were of usual laboratory grade. Collodion particles were prepared by the method of Loeb (15) and washed thoroughly by centrifugation. The silica gel (Patrick) was purified by the method of Reyerson and Clark (24).⁵ It was electrodialyzed, finely ground, and placed in water overnight before using. Aluminum oxide which had been carefully purified and ground in an agate mortar was obtained through the courtesy of Professor R. A. Gortner. The various particles were suspended by shaking in water and adding a suitable small amount to a concentrated protein solution. Under the microscope only three or four particles could be seen in each field.¹ After several minutes the salt was added, then the acid, and lastly water to the volume desired. Unless specified, the final protein concentration was 0.5 per cent. Measurements were carried out using higher concentrations with each type of particle, but no differences could be noted. A tempera-

³ Thanks are due to Dr. Ivon R. Taylor and Mr. Julius C. Abels for carrying out the pH determinations with this electrode.

⁴ Personal communication from Dr. Theodore Shedlovsky.

⁵ Thanks are due to these workers for a supply of this substance.

ture coefficient of 2 per cent per degree was used to bring all values of mobility to 20°C. Room temperatures were usually 22°C.

EXPERIMENTAL

The small open circles in figure 1 are the data of Tiselius for the electric mobility of dissolved egg albumin in $M/50$ acetate buffers at 20°C.

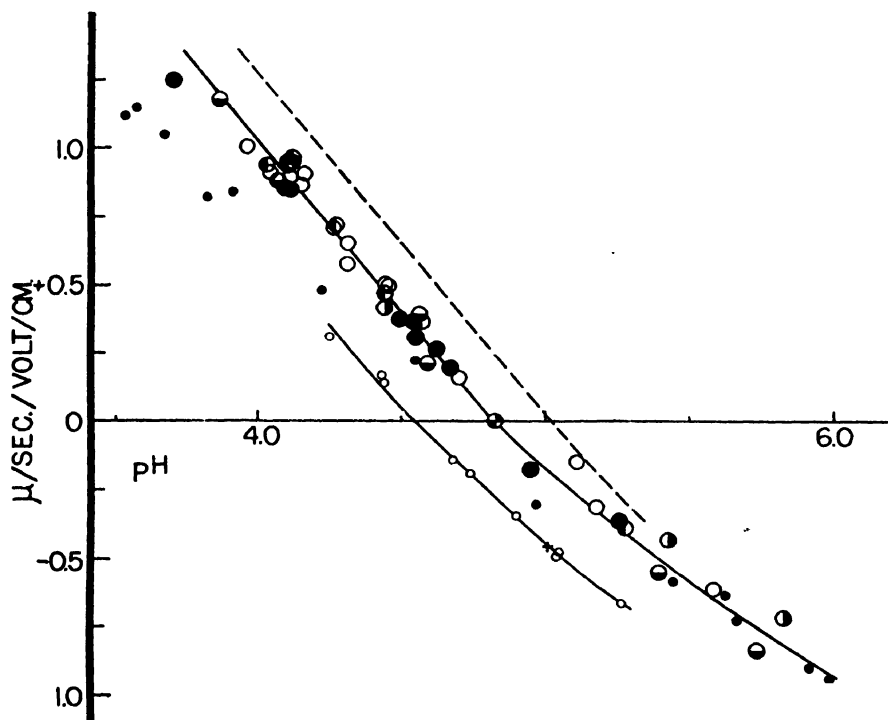


FIG. 1. The small open circles are data of Tiselius for the electric mobility of dissolved egg albumin. The cross is the single point measured under the same conditions by Annetts. Abramson's data for egg albumin adsorbed on quartz particles are plotted as small closed circles. The large open and half-closed circles are similar data of our own obtained with glass, collodion, quartz, mineral oil, and carbon surfaces coated with four preparations of egg albumin (each type of circle represents a separate preparation of egg albumin) in $M/50$ acetate buffers. The large closed circles are results obtained with another preparation coated on quartz in $M/50$ sodium chloride-hydrochloric acid solutions. The dashed line is the smoothed curve for surface-denatured material.

The value given by Annetts has been plotted as a cross on Tiselius' curve. The small closed circles are the data of Abramson for egg albumin-coated quartz particles under these conditions. The other large points are values for the electric mobility of particles of Pyrex glass, mineral oil, carbon, collodion, and quartz when coated with egg albumin and suspended in

M/50 acetate buffer at 20°C. The different kinds of circles indicate the five preparations of egg albumin. No differences could be noted between the behavior of these various types of particles in contact with any of the different egg albumin preparations over the range of pH investigated, nor could any differences be found between the different preparations of the protein when coated on any one of these particle types; this was tested in each case. Although space does not permit any indication of the vari-

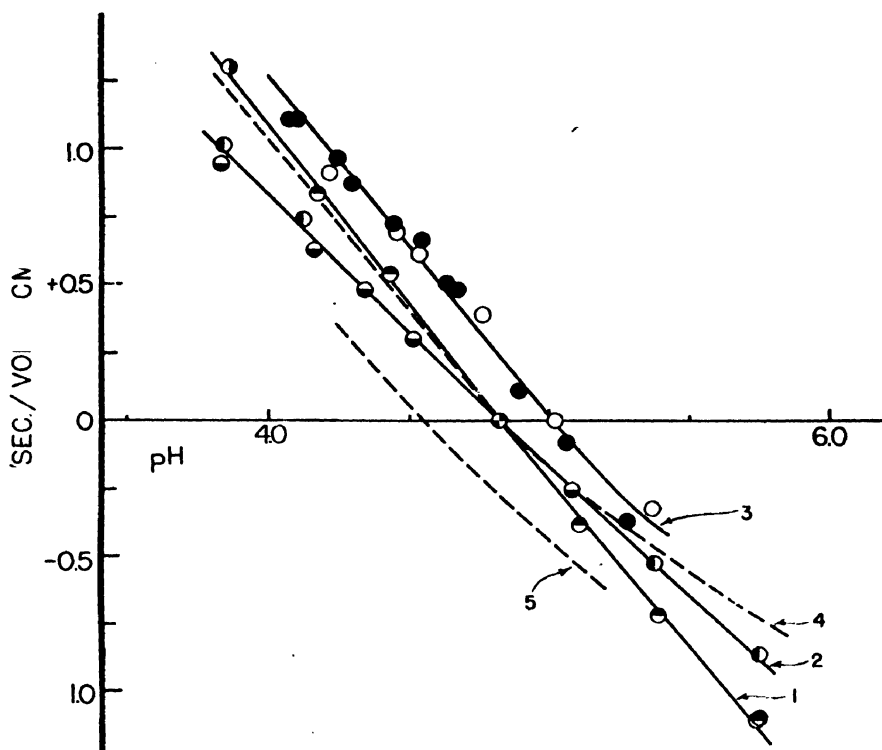


FIG. 2. Curve 1, aluminum oxide particles coated with two preparations of egg albumin; curve 2, the same preparations on silica gel; curve 3, surface-denatured egg albumin,—open circles, freely suspended, closed circles, adsorbed on quartz; curve 4, egg albumin on "inert" surfaces (from figure 1); curve 5, smoothed curve of Tiselius' data.

ous underlying surfaces in figure 1, measurements were distributed fairly evenly over the five particle types. Data for the construction of the smoothed curves in figures 1 and 2 are presented in table 2. It will be noted that the points follow a nearly linear course from pH 3.8 to pH 4.82, the isoelectric point.⁶ From here the curve remains parallel to that of

⁶ The positions of the isoelectric points discussed in this paper were determined in all cases by finding the pH of least motion and also by interpolation of the mobility curve. No differences between these two methods were ever noted.

Tiselius by bending slightly toward the base line. A separate series of observations was carried out with completely different apparatus, using quartz coated by an additional preparation of egg albumin (0.76 per cent) and suspended in sodium chloride-hydrochloric acid solutions likewise at a constant ionic strength of 0.02. In this case, pH was measured by the glass electrode. These data are plotted as large closed circles (figure 1). The agreement is excellent, emphasizing the importance of ionic strength rather than total buffer molarity in influencing the mobility. The position of the isoelectric point was identical, within the limits of error, with the data in the acetate buffer.

The behavior of albumin-coated silica gel is shown in curve 2 of figure 2. It will be noted that the mobilities are significantly affected by the underlying surface. Silica gel is not only extremely hydrophilic but also possesses an ionogenic surface. Another surface of this type but positive in

TABLE 2

Data for the construction of smoothed curves in figures 1 and 2

NORMAL EGG ALBUMIN*				EGG ALBUMIN ON SILICA GEL		EGG ALBUMIN ON Al_2O_3		SURFACE EGG	
pH	v †	pH	v	pH	v	pH	v	pH	
4.00	+1.02	5.40	0.50	4.00	+0.83	4.00	+1.08	4.00	+1.27
4.82	0	5.60	0.65	4.82	0	4.82	0	5.02	0
5.00	-0.17	5.80	0.79	5.80	-0.93	5.80	-1.20	5.20	-0.22
5.20	0.34	6.00	0.92					5.40	0.40

* Adsorbed on glass, quartz, collodion, mineral oil, and carbon.

† In μ per second per volt per centimeter.

charge is aluminum oxide (Al_2O_3). Aluminum oxide when coated with egg albumin yielded the same isoelectric point as the other surfaces (curves 2 and 4). As in the case of silica gel, the curve is composed of two straight lines radiating from the isoelectric point (curve 1, figure 2). The position of the curve, while close to that of curve 4 on the acid side of the isoelectric point, was markedly divergent at higher pH values.

It has been mentioned that one preparation which had become opalescent had a high gold number but behaved anomalously from the other preparations. Quartz particles placed in buffers containing this preparation (0.5 per cent protein) were isoelectric at pH 5.02, although the mobility curve was parallel to that of the other preparations on its acid side (large closed circles, curve 3, figure 2). Upon filtration all traces of this exceptional behavior disappeared. Dilute egg albumin from another preparation which had not required filtration was shaken to produce surface-denatured egg albumin. Particles of this denatured material suspended in buffers (without additional particles) yielded the data

plotted as large open circles in curve 3 of figure 2. These too were iso-electric at pH 5.02. As usual, particles moved independently of size and shape. It appears probable that the opalescent solution contained traces of surface-denatured protein; these, being strongly surface-active (7), were selectively adsorbed. The data indicate that normal albumin does not coat surface-denatured albumin which has been formed at an air-water interface and subsequently dispersed by shaking, or if it does, it in turn is denatured. This hypothesis is borne out by the fact that the one set of data was obtained with quartz in 0.5 per cent albumin, whereas the undenatured albumin in the final dilutions of purposely denatured material could not have been higher than 0.008 per cent if none had been denatured, yet both curves are the same. The presence of undenatured

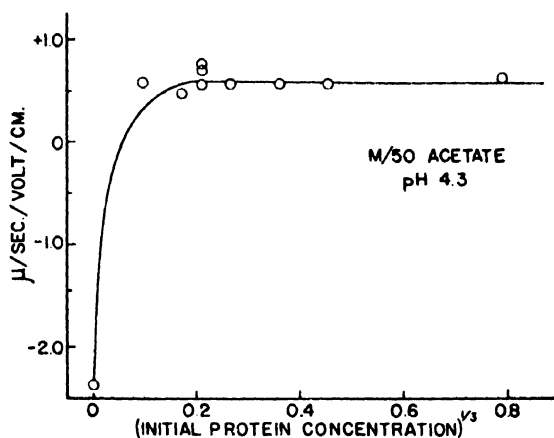


FIG. 3. Electric mobility of glass plotted against cube root of initial protein concentration in per cent.

protein in the surface-denatured sample was demonstrated by filtering off the coagulated material and heat-denaturing the clear filtrate.

The change in mobility with concentration of the initial protein solution is shown in figure 3. This experiment was performed in a cell which had first been filled with strong protein solution, then rinsed with water. As will be noted, the curve is perfectly regular and smooth, showing no exceptional behavior at low concentrations beyond a tendency for higher variation between mobilities at concentrations where the coating is presumably incomplete. This is similar to the curves of Freundlich and Abramson (9) for crude egg albumin.

Neurath (22) has pointed out that egg albumin spread in a surface trough requires up to seven minutes to become surface-denatured. Special observations to test this point, made within a minute after adding glass particles to the protein solution (pH 4.2), showed no progressive

changes in mobility with time. The order of adding the reagents was found to have no effect. Evidently the protein coating is at equilibrium with the medium very soon after its formation.

DISCUSSION

The isoelectric point

Our value for the isoelectric point of egg albumin is identical with that found by Smith at the same ionic strength, yet the mobility curve is shifted 0.27 pH unit from Tiselius' curve for dissolved protein. Although Tiselius' value for the isoelectric point is pH 4.55, his value for the isoionic point is pH 4.76. Smith, however, found complete agreement (within 0.01 pH) between the isoionic and isoelectric points over a wide range of salt and protein concentrations. This makes it possible that a reinvestigation of the subject, using both macro- and micro-electrophoresis techniques on the same highly purified sample, would yield results more in agreement. If, however, Tiselius' data are correct, it is rather remarkable that the same shift in isoelectric point is produced for all the adsorbing surfaces. A simple explanation for this shift based on electrical adsorption is not available, as two of the surfaces were positive (carbon and aluminum oxide) and the rest negative, yet all have the same isoelectric point when coated with egg albumin.

On the basic side of the isoelectric point, the agreement between our results with quartz and those of Abramson is excellent. Barring a few of his points at low mobilities where measurements cannot be carried out with the same accuracy, his curve could be considered as having the same isoelectric point as ours but diverging in slope on the acid side. The results of Abramson were carried out with quartz particles which had been specially cleaned by long boiling with concentrated hydrochloric acid and which had been in contact with water for several years.⁷ As this material was no longer available, quartz was treated with hydrochloric acid and washed, but no change in protein behavior was observed. Since Abramson's results were based on two samples of egg albumin (crystallized four times and water-clear⁷), it is altogether possible that long soaking had hydrated the surface of his quartz similar to silica gel. Indeed, our silica gel curve (figure 2, curve 2) is within the limits of error of Abramson's points (10 per cent⁷) so that the difference cannot be considered significant.

Nature of the surface film

Hitchcock (12) has shown that egg albumin is adsorbed as a film of polymolecular thickness on porous collodion membranes by demonstrating

⁷ Personal communication from Dr. Abramson.

that a weighable amount, far in excess of that needed for a monomolecular layer, is present. It is therefore not surprising that the underlying surface has so little effect on the mobility. It should be mentioned that the theoretical possibility of the underlying surface affecting electric mobilities of proteins was pointed out by Halpern (10).^{8,9} The difference between the effect of the "inert" surfaces on one hand and silica gel or aluminum oxide on the other can scarcely be explained by chemical union of amino or carboxyl groups with the surface, for the isoelectric point is unchanged; moreover, aluminum oxide is basic and silica gel acidic.

Consideration of the modified Debye approximation (2, 4),

$$\pm v = \frac{\pm Q}{C\eta r(\kappa r + 1)} \quad (6)$$

where v = electric mobility, Q = net charge, C = proportionality constant, r = radius, η = coefficient of viscosity, $\kappa = f$ (ionic strength), shows that addition of a constant charge to Q (equivalent to removal or addition of electrons by electrical adsorption) would shift the isoelectric point but leave the curves parallel if the radius remained constant. A change in the effective radius (here probably that of the protein molecule (2, 4, 21)) would rotate the curve on its axis, leaving the isoelectric point unchanged.¹⁰ We are inclined to look for an alteration of this kind as an explanation of the effect of silica gel and aluminum oxide.

It was discovered by Loeb (16) that after collodion particles had been placed in a strong solution of egg albumin, a few drops of the suspension added to a large volume of salt solution showed properties greatly altered from those of dissolved protein. The collodion was precipitated at concentrations far below those needed to precipitate dissolved egg albumin. Loeb concluded that these experiments indicated that egg albumin adsorbed on quartz was surface-denatured. If this were so, it might be expected that the innermost layer would be different in charge density from the outer coating, if surface denaturation at a solid surface produces a film oriented in the same direction as at an air-water interface. Yet figure 3 shows no changes in mobility with increasing protein concentration once the surface is coated. Particles of glass treated as in Loeb's experiments gave exceedingly variable mobilities in buffer solutions,

⁸ Dummett and Bowden (8) have maintained that hemoglobin likewise shows the influence of the underlying surface. See, however, references 4, 19, and 32.

⁹ Gelatin apparently is not so easily affected by positive and negative ionogenic surfaces, for Hazel and King (11) find that the mobility curves of gelatin-coated manganese dioxide and ferric oxide are identical.

¹⁰ Under our conditions, the value of C is probably near 6π (2, 4). A slight change in r would probably produce a change in C of secondary order of magnitude.

indicating that under these conditions the surface film is no longer complete.

Evidently the isoelectric point (pH 5.02) or the curve shape of surface-denatured albumin when suspended in buffer is not affected by its adsorption nor does it tend to adsorb egg albumin in an unaltered state. The possibility exists that such a surface may progressively denature new layers as they are adsorbed. The presumptive shift of isoelectric point from pH 4.55 to pH 4.82 on adsorption on "inert" surfaces indicates that only about two polar groups per molecule are lost by this process. Moreover, if denatured, the egg albumin surfaces which are isoelectric at pH 4.82 are not identical with egg albumin denatured at an air-water interface.

The shift of isoelectric point to higher pH values by this type of denaturation was to have been expected from the results of Bull and Neurath (7), who found that between pH 4 and pH 6 the pH of a solution of egg albumin increases 0.6 pH unit incidental to surface denaturation. This would indicate a binding of acid or a release of base corresponding to a shift in charge, as discussed in connection with equation 6. It is, however, probable that the protein molecule spreads out during denaturation (7, 18, 22) so that equation 6, derived for a sphere, would no longer apply. The results also agree with the concept of Mirsky and Pauling (18) that, on spreading out, a protein releases paired carboxyl and amino groups by breaking hydrogen bonds. As they suggest, this would shift the isoelectric point upward on the pH scale.

SUMMARY

1. A combination of Komagata's expression for the position of the stationary level in flat closed electrophoresis cells with the theory of Smoluchowski permits the true mobility to be calculated from measurements at the center of the cell, providing that the cell wall and particle surfaces are the same in composition.

2. Highly purified solutions of egg albumin adsorbed on "inert" surfaces such as quartz, glass, mineral oil, carbon, and collodion, exhibit the same isoelectric point at pH 4.82 in *M*/50 acetate or sodium chloride-hydrochloric acid solutions. This isoelectric point confirms the results of Smith.

3. The electrophoretic mobility-pH curve is identical for all of these surfaces when coated with any of five preparations of egg albumin and suspended in *M*/50 acetate or sodium chloride-hydrochloric acid solutions of constant ionic strength.

4. When egg albumin is adsorbed on silica gel or aluminum oxide particles, its isoelectric point remains at pH 4.82 but each curve is influenced by the nature of the underlying surface.

5. Surface-denatured egg albumin freely dispersed or adsorbed on

quartz is isoelectric at pH 5.02 in *M*/50 acetate buffers. The electric mobility curve is correspondingly displaced, but is parallel to that for native egg albumin on "inert" surfaces.

6. The nature of the surface film of egg albumin is discussed in the light of these results.

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STUDIES ON SILICIC ACID GELS. VIII

THE TIME OF SET OF GELS CONTAINING STRONG ACIDS

CHARLES B. HURD, KENNETH J. FREDERICK, AND
CHARLES R. HAYNES

Department of Chemistry, Union College, Schenectady, New York

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INTRODUCTION

The time required for the setting of a sol of hydrated silica, giving what we call a silicic acid gel, has been found to depend primarily upon the concentration of silica, the temperature, and the hydrogen-ion concentration. A careful study of the relation between time of set, as we have defined it, and the temperature on the one hand and the hydrogen-ion concentration on the other, for gels produced from solutions of sodium silicate and acetic acid, has already been reported from this laboratory in previous papers of this series (3, 4, 5). In addition, the same study, extended to other weak acids,—citric, succinic, and tartaric, —was reported by Hurd (1).

We have suspected that the weak acids, because of the buffering effect of the sodium salts formed during the reaction with the sodium silicate, give a practically constant hydrogen-ion concentration. Hence the reaction of setting, whose rate manifestly depends upon the hydrogen-ion concentration should, and does, proceed at a more uniform rate than it would in a solution whose hydrogen-ion concentration was not so constant. In order to investigate this phenomenon, we have made a study of the time of set of gel mixtures produced by mixing solutions of sodium silicate with solutions of the strong acids, nitric, hydrochloric, and sulfuric. The effect of temperature and of hydrogen-ion concentration upon the time of set of such mixtures is reported in this paper.

EXPERIMENTAL

The gel mixtures were produced in the same way as those reported in the former papers of this series. A large volume of sodium silicate solution was made by dilution of "E" brand silicate, produced by the Philadelphia Quartz Company, with recently boiled, distilled water. The large amount ensured uniform concentration throughout this investigation. This solution titrated 1.255 *N*, as equivalent in sodium hydroxide against

standard sulfuric acid using methyl orange. Standard 2.0 *N* solutions of nitric, hydrochloric, and sulfuric acids were prepared.

During the studies on gels containing acetic acid, a considerable variation in the concentration of acetic acid was made. This was necessary in order to make a suitable variation in the hydrogen-ion concentration, owing to the buffering effect of the sodium acetate formed. Here, however, in mixtures of solutions of a strong acid and sodium silicate, the hydrogen-ion concentration changes very rapidly near the neutral point, just as occurs during the neutralization of a strong acid with a strong base. This rapid change in hydrogen-ion concentration made it impossible to measure out two different mixtures which would have the same hydrogen-ion concentration. Accordingly, double mixtures were made in each case, one half of which was used to measure pH and the other half to measure the time of set. By attempting to measure the same amount of acid and of silicate for each trial, we secured a sufficient variation of pH; in fact, some mixtures came on the alkaline side and were discarded, since this study was confined to acid gel mixtures. For the mixtures with lowest pH a little more acid was used. These mixtures could be made up by measure to within a few tenths of a pH unit.

The amount of the acid solution, nitric, hydrochloric, or sulfuric, required to neutralize 50 cc. of the 1.255 *N* silicate solution was determined by a titration. This would be almost the same for each acid. The mixtures were made by placing this amount of acid solution, measured from a special pipet or from a buret, in a beaker and adding enough distilled water to give exactly 110 cc. In another beaker was placed 50 cc. of the silicate. The two beakers and contents were placed in a thermostat whose temperature was just far enough below the temperature of the thermostat used for determining the time of set so that the temperature of the mixture would rise to exactly the correct temperature. This heat is provided by the immediate ionic reaction. It varies a little, but is approximately 1.4°C. When the acid and the silicate solutions had attained the temperature of this temporarily used thermostat, they were mixed, the procedure always being to pour the silicate into the acid and then to pour the mixture back and forth several times. Thereupon the mixture was divided, 80 cc. being poured into a 100-cc. Pyrex Griffin beaker, which had been held in the thermostat used for the determination of the time of set. The other 80 cc. was used to determine the pH at 25°C. by the quinhydrone method, using a bright platinum wire. This has been shown to be accurate by Hurd and Griffeth (2).

The time of set was determined by the tilted-rod method, as described by Hurd and Miller (4). It is true, as Prasad and Parmar (8) have remarked, that the tilted-rod method for determination of the time of set gives the time for a certain fraction of the process of gelation to occur.

Nevertheless, we have found from a great many determinations that the method, empirical as it is, gives very reproducible results.

The thermostats have been described in other papers in this series.

THE VARIATION IN THE HYDROGEN-ION CONCENTRATION

With these strong acids the hydrogen-ion concentration of the mixtures was found to show from an appreciable to a considerable change from the

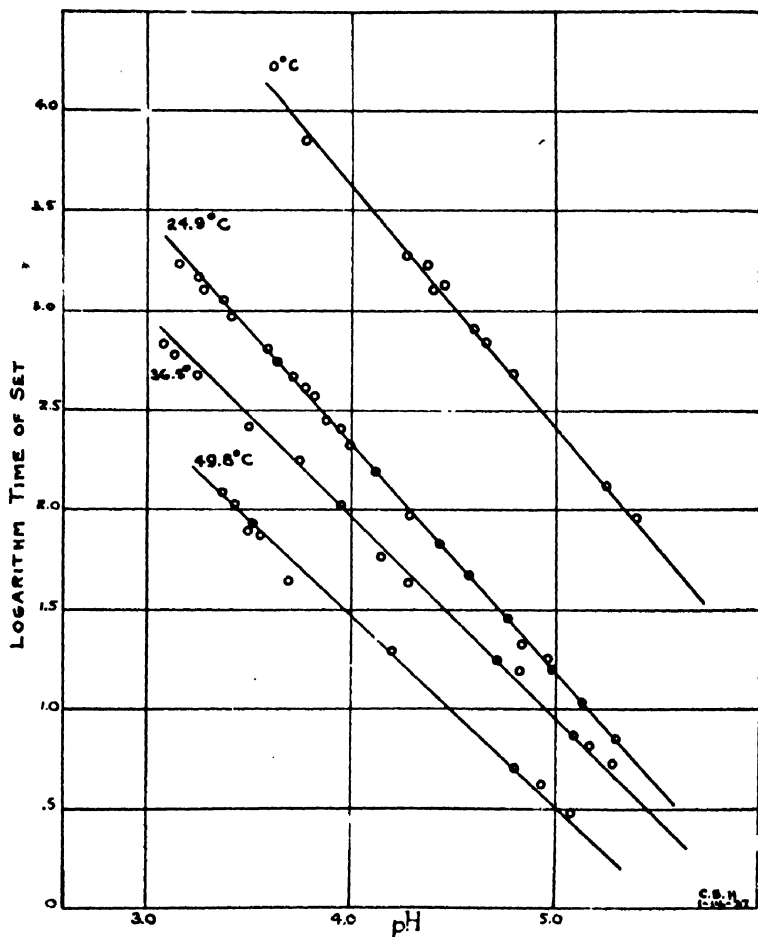


FIG. 1. Relation between logarithm of time of set and pH for gel mixtures using hydrochloric acid

time of mixing until the gel had set. The change probably continued in all cases for some time after the gel had set, as was verified by sufficient experiments. The change, after setting had occurred, was very small, however, and naturally could be disregarded, so far as its effect upon the time of set was concerned, since the gel had already set.

The change was least with the gels of higher hydrogen-ion concentration, as would be expected. Such gels reached a constant pH before setting, but as the pH approached 7 greater changes occurred. These gels set more quickly and in some the pH was not constant until some time after the gel had set. We have measured the pH frequently for each mixture, but record here only the constant value.

This change in the pH has very real significance and will be treated fully later in another paper. As a rough comparison, the pH change at pH = 3.0 would be 0.2 pH unit or less, while for pH = 6.0 a change up

TABLE 1

Logarithm of times of set in minutes as a function of pH, temperature, and acid used

pH	LOGARITHM OF TIME OF SET IN MINUTES AT				
	0°C.	24.9°C.	35.3°C.	36.5°C.	49.8°C.
Nitric acid gels					
3.0	4.70	3.44	2.92		2.38
3.5	4.09	2.90	2.44		1.92
4.0	3.48	2.36	1.96		1.46
4.5	2.86	1.82	1.49		1.01
5.0	2.26	1.28	1.02		0.56
Hydrochloric acid gels					
3.0	4.89	3.48	2.96	2.39	
3.5	4.26	2.90	2.46	1.98	
4.0	3.64	2.34	1.96	1.46	
4.5	3.03	1.76	1.46	0.99	
5.0	2.41	1.18	0.98	0.51	
Sulfuric acid gels					
3.0	5.40	3.32	2.84		2.16
3.5	4.72	2.82	2.42		1.76
4.0	4.04	2.30	2.00		1.38
4.5	3.36	1.79	1.58		1.00
5.0	2.67	1.28	1.16		0.62

to 0.6 pH unit was observed. No great difference was noted in this respect between the three strong acids used.

EXPERIMENTAL RESULTS

The many data for the time of set as a function of the pH for each of the three acids at each of four temperatures were plotted on curves such as the one shown by figure 1. For these mixtures the concentrations are, in gram-moles per liter: Na = 0.392, SiO₂ = 0.638, and acid added very slightly more than equivalent to the sodium. This very slight excess

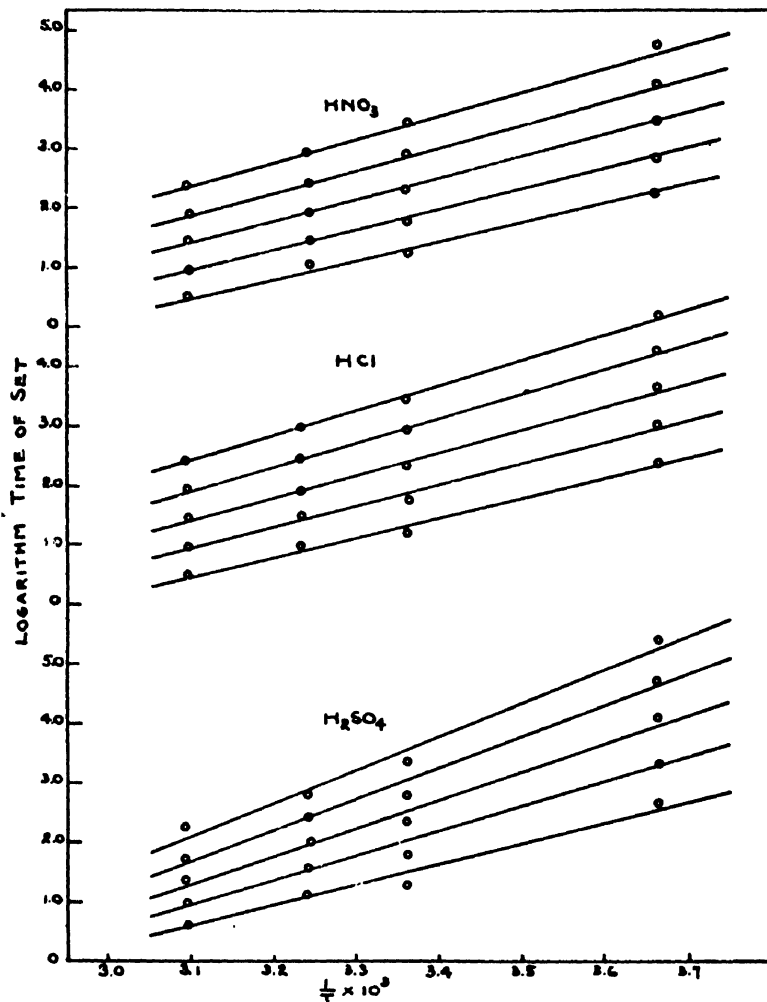


FIG. 2. Relation between logarithm of time of set and reciprocal temperature for gel mixtures which contain the strong acids

TABLE 2

The heat of activation of the setting of silicic acid gels made with strong acids

pH	NITRIC ACID	HYDROCHLORIC ACID	SULFURIC ACID
	Q	Q	Q
	calories	calories	calories
3.0	18,200	20,280	26,550
3.5	17,300	18,870	24,130
4.0	16,400	17,630	21,630
4.5	15,380	16,470	19,070
5.0	14,570	15,230	16,510
Mean	16,370	17,700	21,580

gave, as explained before, sufficient variation in the hydrogen-ion concentration. The hydrogen-ion concentration in each is shown by the pH.

From the three curves data were interpolated to give the results shown by table 1. These data show the effect of temperature upon times of set for five series of pH values for each acid, which would have been impossible to obtain by direct mixing, as has been explained.

These data were plotted on large graph paper with the logarithm of time of set as ordinates against reciprocal absolute temperature as abscissae. Figure 2 shows a composite plot.

As previously shown by Hurd and Miller, the slopes of these curves multiplied by 2.30 R give a quantity called the heat of activation. The values obtained for this quantity are given in table 2.

DISCUSSION

In order to explain the data of table 2, it will be necessary to refer briefly to the previous work which has been reported, upon the effect of temperature on the time of set of various silicic acid gel mixtures.

The original investigation, upon the effect of temperature on the time of set of silicic acid gel mixtures produced by mixing solutions of sodium silicate and acetic acid, has been mentioned (4). The data showed that this quantity, which we have called the heat of activation, remained practically constant regardless of the kind of sodium silicate used or of the acidity, so long as the gel mixtures were acid.

The following investigation, which included also the weak acids, citric, succinic, and tartaric, and in which a correction was made for the small initial rise of temperature (about 1.4°C.) showed again that the heat of activation was very nearly constant (1). While the agreement for citric, acetic, and succinic acids fell within the experimental error, the value for tartaric acid was a little larger than could be explained on the basis of experimental error. The average values for acetic, citric, succinic, and tartaric acids were, as reported, 17,140, 16,940, 17,190, and 17,530 calories, respectively.

While we may, therefore, feel considerable confidence in viewing this heat of activation as a very fundamental constant, whether different types of sodium silicate or different weak acids are used, the fact that the strongest acid of the four, tartaric acid, showed a larger value than could be explained, deserved an explanation.

A glance at table 2 shows this more strikingly. There is much more variation in the heat of activation for any one strong acid than was shown by the weak acids. We should note here, also, that a wider range of pH was covered with the strong acids. In addition, the differences between the strong acids are much greater than were shown by the weak acids.

The explanation of this apparent discrepancy between the results shown

by the weak and the strong acids lies in the fact, reported in this paper, that during the process of setting the gel mixtures have shown from a measurable to a considerable change in pH. Since, as Hurd, Raymond, and Miller (5) have shown, the velocity of the setting reaction is inversely proportional to the hydrogen-ion concentration, these gel mixtures using strong acids are undergoing a reaction whose velocity varies. This is the more evident, since in mixtures of sodium silicate and a strong acid there is little buffering power, while in the mixtures made from the weak acids, the presence in the mixture of the sodium salt of the weak acid and the excess weak acid gives excellent buffering power.

While it might be possible to add buffering mixtures to these gel mixtures containing the strong acids, in order to obtain a constant pH, such a process would prove undesirable. The systems would be much more complicated than our present mixtures and, as we are aware, simplification rather than complication should be sought in these already complicated solutions.

To proceed in the other direction, the very pure silica sols produced by the oxidation of silane by Kargin and Rabinovich (6) would prove a very interesting field for these temperature-time of set studies. This is impossible, unfortunately, owing to the fact that the formation of the original sol of hydrated silica or silicic acid occupies a considerable time. It is essential that the sol be prepared within a few seconds.

The whole study of the change in the pH of the sols during setting is of the greatest importance and will be reported from this laboratory in a paper to follow. It is possible for us to borrow from the proposed paper sufficient data to show why we may expect the energy of activation to vary in these mixtures involving strong acids. In addition, this variation of the hydrogen-ion concentration bears directly upon our theory of the mechanism of setting.

The present theory for the setting of these gels of silicic acid is derived from the statement of Mylius and Groschuff (7) and others, that in the instantaneous reaction of the acid with the sodium silicate, a simple silicic acid is formed. This is probably a monosilicic acid. Such an acid, according to Treadwell and Wieland (9), shows an appreciable ionization, since the value for its first ionization constant, K , equals $10^{-9.7}$. According to the theory, this simple silicic acid forms long chains of silicic acids by condensation. These acids must become weaker, owing to their increasing molecular weight, and also owing to the fact that the more active hydrogens have been removed during the condensation. It is probable that larger and larger groups condense as the process goes on. Thus the setting appears to take place very suddenly, regardless of whether one is observing the viscosity, tensimeter reading, elasticity, scattering of light, or any one of other characteristic properties, although

a relatively long preliminary or induction period has passed. When these groups have become sufficiently large, there is probably little, if any, acidic ionization giving hydrogen ions. Kargin and Rabinovich have reported a pH of 7.0 for their pure silica sols.

The disappearance of this acid and the corresponding decrease in the hydrogen-ion concentration through its effect upon the specific reaction rate undoubtedly is the cause of the variation in these results for the energy of activation. It is doubtful whether we shall be able to measure this quantity in the mixtures containing the strong acids with any greater accuracy. We may say, therefore, that it is our belief that the energy of activation for the setting reaction for silicic acid gels in acid mixtures is very close to 17,100 calories.

It is difficult to give a true idea of the meaning and significance of this energy of activation. If we use it in a purely descriptive sense, we may say that it is a constant by means of which we can calculate the time of set for any given mixture at any reasonable temperature. This constant, naturally, has the dimension of calories.

If we attempt to attach more theoretical significance to this "energy of activation," we must call attention again to the theory that the condensation takes place between two molecules which come into sufficiently close contact so that water may split off. Although at first these molecules are undoubtedly monosilicic acid, as the process continues larger and larger groups must meet and condense. The chances for a condensation resulting from a collision are greater the greater the activity of these super-molecules. It is probable, therefore, that we may apply Arrhenius' idea to this reaction, and that the activity of the groups depends upon the energy of activation.

SUMMARY

The time of set has been determined for a large number of silicic acid gel mixtures, produced by mixing solutions of sodium silicate and either hydrochloric, nitric, or sulfuric acid.

The temperature was varied. The pH was measured in each case.

A variation in the heat of activation of the setting reaction was found, both at different pH values and for the different strong acids.

For these strong acid-gel mixtures, a variation was shown in the pH value as the setting proceeded. This is different from the cases where weak acids have been used.

A discussion is presented of the bearing of these data upon the theory of setting, which assumes that the simple silicic acids condense into polyacids and finally into very complex chains through the splitting out of water. The data substantiate the theory.

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THE SOLUBILITIES AND ACTIVITY COEFFICIENTS OF LANTHANUM IODATE IN CONCENTRATED SALT SOLUTIONS AT 25°C.

J. N. PEARCE AND W. C. OELKE

Division of Physical Chemistry, The State University of Iowa, Iowa City, Iowa

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The effect of one salt, in solution, upon the solubility of another salt has long been an accepted method for the study of the properties of solutions, and for the determination of activity coefficients. This field has been well covered in the case of uni-univalent salts at low concentrations, but little work has been done with saturating salts having high valence ions. Almost no work has been done in concentrated solutions.

W. D. Harkins and W. T. Pearce (6) have determined the solubility of lanthanum iodate in water and in dilute solutions of several salts. They have interpreted their data on the basis of the stepwise partial dissociation of lanthanum iodate.

La Mer and Goldman (7) have studied the solubility of lanthanum iodate in various aqueous salt solutions by the leaching method. They give two values for the solubility of the iodate in water, neither of which agrees with that of Harkins and Pearce. Their work was done in dilute salt solution, except in the case of potassium chloride where a 2.0 molar concentration was reached. Interpreting their results with reference to the Debye-Hückel limiting law, they find increasing negative deviations with increasing concentration of lanthanum nitrate and potassium chloride. At low concentrations the curves for these salts fuse into that of the limiting law, while with potassium sulfate solutions as solvent, the curves show radical positive deviations with no sign of fusion. This phenomenon was previously observed by Brönsted and Peterson (2), and has since been called the "unsymmetrical valence type effect."

La Mer and Mason (10) find similar positive deviations using cobalt-ammines as saturating salts, while Peterson and Meyers (12), with copper iodate, find positive deviations with potassium sulfate solvent solutions but not with magnesium sulfate.

The aim of the present work has been to redetermine the solubility of lanthanum iodate in pure water, and to extend the study of the solubility of lanthanum iodate in solutions of typical salts up to concentrations approaching saturation.

MATERIALS

The lanthanum iodate was prepared by precipitation, following the method of La Mer and Goldman (7). The prepared salt was not allowed to dry, but was kept under water until used. Some of the lanthanum iodate used with potassium chloride solutions was subsequently examined under a micrometer microscope. The particles were irregular in shape and microscopically they showed no definite crystalline form. The x-ray pattern, however, showed crystalline structure. The mean dimensions of the smallest particles were 0.0098 mm. x 0.0073 mm., the largest particles being five to eight times this large. The salts used in preparing the solvent solutions were recrystallized at least twice, the last time from conductivity water. Sodium oxalate from the Bureau of Standards was used as the primary standard to which all analytical data were referred.

METHOD

The work of La Mer and Goldman in dilute solutions was done by the leaching method originated by Brönsted and La Mer (1). An attempt was made to use this method for the determination of solubilities in concentrated solutions, but it seemed impossible to obtain consistent results in this case. Accordingly, this method was abandoned and a rotating shaker was used. In determining solubilities with this apparatus, a generous portion of the lanthanum iodate paste was washed several times with portions of the solvent solution and finally transferred to duplicate oil-sample bottles with the bulk of the solution. The bottles were then clamped to the shaker and rotation started.

After a minimum of two weeks' rotation at 25°C. the bottles were removed from the shaker and suspended near the surface of the water in the constant-temperature bath. The suspension was allowed to settle overnight and the clear solution siphoned into similar bottles also held in the bath. After at least three hours more of settling, the supernatant liquid was again transferred, this time to two dry 250-ml. flasks. Completeness of settling was checked on each solution by means of the Tyndall effect from the beam of a small arc lamp. If more than a very slight cone was visible, the solutions were allowed to settle until they were optically clear.

The analyses of the saturated solutions for iodate ion were made in triplicate, by titration with standard sodium thiosulfate solution of the iodine liberated according to the reaction:



In the analysis, the method of La Mer and Goldman (7) was substantially followed. The best of modern analytical technique was observed

at every step. Carefully calibrated pipets and Normax volume burets were used.

Since in the late afternoon the blue color of the sky interfered with correct determination of the starch-iodine end point, all titrations were carried out under artificial light. The light, which struck the solutions from the top and side, was furnished by a 40-watt. frosted bulb, backed by a reflector and covered by a ground glass. By this means it was possible to maintain a precision of two parts per thousand or better in all titrations.

APPARATUS

The rotating shaker, mentioned above, consisted of a 12-inch brass disc fixed to a brass shaft which ran in brass bearings suspended from an angle iron frame. On each side of the disc were eight hinged bands by which sixteen 200-ml. oil-sample bottles could be clamped to the disc. The bottles were arranged with their necks toward the common center. Owing to the slight taper of the bottles, the squeezing effect of the bands tended to force the stoppers against a concentric brass ring which prevented their leaking. The whole assembly was submerged in a specially constructed water bath. This bath was thermostated to $25^{\circ}\text{C} \pm 0.01^{\circ}$ by means of a large mercury regulator, supersensitive thermionic relay, and electric heater. The shaker was rotated at 35 R.P.M. by means of a rubber and fabric vee belt running from a countershaft above the water to a large pulley on the shaker shaft. The entire shaker mechanism was hinged so that it could be swung out of the bath for inspection and changing bottles.

THEORY

The phenomenon of solubility may be approached from either of two standpoints. The first is the kinetic viewpoint, from which one strives to explain the observed effects from the individual behavior of the ions and molecules. The second is the thermodynamic approach which systematizes the field.

The discovery by means of x-rays of the ionic structure of crystals has necessitated a rearrangement of the kinetic picture of solubility. A crystal of a salt, such as lanthanum iodate, must be thought of as a space lattice of lanthanum and iodate ions. The pattern of ions in this space lattice has not been worked out to date¹, yet it must be such that the electrical attractions between the oppositely charged ions are satisfied. When such a crystal is placed in a polar solvent, as water, water dipoles are attracted

¹ Dr. E. S. Gantz of this laboratory has kindly made for the author an x-ray powder diffraction picture of the lanthanum iodate used. This analysis indicates that lanthanum iodate crystals have the ionic type of lattice.

by the unbalanced electrical fields at the crystal boundaries. This orientation of water dipoles around the crystal has a tendency to weaken the attractive forces holding the ions of the crystal together. The result is that the kinetic motion of some of the surface ions is sufficient to free them from the attraction of their neighbors and they escape into the body of the liquid. Once the ions have escaped from the crystal, water dipoles will orient themselves completely around the ions. The external fields of these ions are thus largely satisfied by this water sheath. G. W. Stewart (14) contends that sufficient attractive forces still exist between dissolved ions to give a "structure" to the solution. This "structure" may be considered as a mobile, widely spaced, ion lattice similar perhaps to that in the crystal itself.

The process of solution will continue, following the above mechanism, until the condition which we know as saturation has been reached. In this state a condition of equilibrium exists between the solid and the dissolved solute. Evidently the forces causing the escape of ions from the crystal have been balanced by attractive forces between the ions working in the other direction.

EFFECT OF SALTS

The macroscopic effect of salts upon the solubility of a substance, as experimentally observed, is well known. The presence of salts with a common ion tends to decrease the solubility of a salt in water solution. When no common ion is present, an increase in solubility of the saturating salt is observed. The actual mechanism behind the phenomenon, however, can only be postulated.

According to Butler (3), the ions of salts mutually affect each other in two ways: (1) directly, owing to the forces between their electrical charges, whereby they attract ions of opposite charge and repel ions of like charge; (2) indirectly, through the effect of their electrical fields upon the molecules of the solvent. A suitable theory of solubility must take both of these effects into consideration. The latter effect, i.e., the orientation of water about the salt ions in solution, has already been discussed. It would lower the mole fraction of free solvent water in the solution, and hence have a depressing effect upon the solubility. The increase in solubility, observed in the present case, must obviously be due to the first of these forces mentioned.

In order to account for this "salting-in" effect, let us visualize conditions in a potassium chloride solution saturated with the salt, lanthanum iodate. If we consider both salts to be completely ionized, the following species will be present: La^{+++} , K^+ , H_3O^+ , IO_3^- , Cl^- , OH^- , H_2O . According to Debye and Hückel (4), a given ion will, at any time, be surrounded by an ionic atmosphere in which ions of opposite charge predominate. Thus, a

lanthanum ion will be surrounded by an atmosphere in which iodate, hydroxide, and chloride ions predominate, while an iodate ion will be largely surrounded by potassium, oxonium, and lanthanum ions. In order for a lanthanum iodate crystal to grow, lanthanum and iodate ions must be able to settle out on the crystal lattice. If the ionic atmosphere around the lanthanum ions is composed largely of iodate ions, the chance of lanthanum and iodate ions settling out upon the crystal lattice of some adjacent lanthanum iodate solid will be comparatively great. Equilibrium with the solution tendency of the crystal will obtain at a low concentration, and we say that the salt has a low solubility. On the other hand, if the residual force fields about the chloride ions are greater than those around the iodate ions, the chloride ions will predominate in the ionic atmosphere of the lanthanum ions. The result of this will be that lanthanum and iodate ions will have less opportunity to settle together upon the solid lattice. The equilibrium will thus be displaced, by the presence of chloride ions, in the direction of increased solubility.

If some other negative ions with greater residual force fields than those of the chloride ions are placed in the solution, they will usurp the place of the iodate ions to a still greater extent. Thus, with sulfate ions present, a still greater increase in the solubility of the lanthanum iodate should be observed.

There is, of course, the possibility of lanthanum and chloride ions or lanthanum and sulfate ions forming lattices of their own under these conditions. This does not take place, however, because the tendency toward solubility is too great, owing in part to the fact that these same chloride and sulfate ions, with their large residual force fields, are too highly hydrated.

Glasstone, Dimond, and Jones (5) give the following relative hydration numbers for negative ions on the basis of the iodide ion as zero:

	HYDRATION NUMBER		HYDRATION NUMBER
$\text{Fe}(\text{CN})_6^{4-}$	75	$\text{C}_2\text{H}_3\text{O}_2^-$	13
$\text{C}_2\text{O}_4^{2-}$	31	Cl^-	10
SO_4^{2-}	26	ClO_3^-	9
$\text{Fe}(\text{CN})_6^{3-}$	23	Br^-	5
F^-	17	NO_3^-	2
CrO_4^{2-}	14	I^-	0

The values were obtained from a study of the salting-out effect. They consider these values a measure of the strength of the electrostatic fields surrounding the ions. Randall and Faily (13) arrange the negative ions in order of decreasing salting-out effect thus: $\text{OH}^- > \text{SO}_4^{2-} > \text{CO}_3^{2-} > \text{ClO}_3^- > \text{BrO}_3^- > \text{Cl}^- > \text{Ac}^- > \text{IO}_3^- > \text{Br}^- > \text{I}^-$. Although the iodate ion

is not mentioned in Glasstone's table, it will probably have no greater value than that of the chlorate ion. It is to be observed in both of these series that the order is $\text{SO}_4^{--} > \text{Cl}^- > \text{IO}_3^-$. It will be shown later that this fact, together with the theory proposed above, easily explains the solubility behavior of these solutions.

There is no doubt a similar effect with reference to the anion of the saturating salt. Experimental evidence, however, points to the fact that in the case of lanthanum iodate, with a high valence cation, the solubility behavior is principally dependent upon the high valence ion. Thus, with a uni-trivalent saturating salt, sulfate solvent salts *have a normal effect* (10).

TABLE 1

The solubilities and activity coefficients of lanthanum iodate in aqueous potassium chloride solutions

MOLALITY OF ADDED SALT	SOLUBILITY OF $\text{La}(\text{IO}_3)_3$ (BY ANALYSIS)	DENSITY AT 25°C. (EXPTL.)	SOLUBILITY OF $\text{La}(\text{IO}_3)_3$ (CALCULATED)	μ MOLAL	$\mu^{\frac{1}{2}}$	$\log \frac{S}{S_0}$	$-\log \gamma_{\pm}$	γ_{\pm}
	<i>moles per liter</i>		<i>moles per 1000 g.</i>					
0.0000	0.0006634	0.99749	0.0006653	0.003992	0.06318	{	0.0953	0.8030
							0.09555	0.8025
0.0010	0.000684	0.99750	0.000686	0.005116	0.07153	0.01347	0.10902	0.7780
0.005	0.000737	0.99776	0.000739	0.009434	0.09713	0.04555	0.14110	0.7226
0.010	0.000786	0.99801	0.000789	0.014734	0.12138	0.07402	0.16957	0.6767
0.050	0.001014	1.00000	0.001019	0.056114	0.23688	0.18508	0.28063	0.5216
0.100	0.001195	1.00243	0.001202	0.107212	0.32743	0.25675	0.35230	0.4443
0.500	0.001919	1.02090	0.001952	0.511712	0.71533	0.46744	0.56299	0.2735
1.000	0.002452	1.04277	0.002531	1.015186	1.00757	0.58021	0.67576	0.2110
2.000	0.003167	1.08268	0.003368	2.020208	1.4213	0.70437	0.79992	0.1585
3.500	0.003898	1.13787	0.004329	3.525974	1.8778	0.81336	0.90891	0.1233

Note: Each of the values given above is the mean of the results from at least two experiments.

DISCUSSION OF DATA

In the present research, the work of La Mer and Goldman (7) on the solubility of lanthanum iodate in potassium chloride and potassium sulfate solutions has been repeated on a molal basis, and carried into a region of higher concentrations. In addition, solubility data have been obtained in the presence of the bi-univalent and bi-bivalent salt types. The solvent salt solutions were made upon a molal basis. The solubilities were first determined on a molar basis, the densities were determined, and the molal solubilities then calculated from these data.

Tables 1, 2, 3, and 4 give the solubilities and activity coefficients of lanthanum iodate in potassium chloride, potassium sulfate, magnesium

chloride, and magnesium sulfate salt solutions, respectively. The solubility of the salt in conductivity water is also given. It is believed that the column headings are self-explanatory.

TABLE 2

The solubilities and activity coefficients of lanthanum iodate in aqueous potassium sulfate solutions

MOLALITY OF ADDED SALT	SOLUBILITY OF $\text{La}(\text{IO}_3)_3$ (BY ANALYSIS)	DENSITY AT 25°C. (EXPTL.)	SOLUBILITY OF $\text{La}(\text{IO}_3)_3$ (CALCULATED)	μ MOLAL	$\mu^{\frac{1}{3}}$	$\log \frac{S}{S_0}$	$-\log \gamma_{\pm}$	γ_{\pm}
	moles per liter		moles per 1000 g.					
0.0000	0.0006634	0.99749	0.0006653	0.003992	0.06318		0.09555	0.8025
0.0010	0.000824	0.99790	0.000826	0.007962	0.08923	0.09421	0.18976	0.6460
0.005	0.001215	0.99847	0.001219	0.022314	0.14936	0.26300	0.35855	0.4380
0.010	0.001488	0.99952	0.001493	0.038958	0.19738	0.35096	0.44651	0.3577
0.050	0.002568	1.00554	0.002581	0.165480	0.40679	0.58873	0.68428	0.2069

Note: Each of the values given above is the mean of the results from at least two experiments.

TABLE 3

The solubilities and activity coefficients of lanthanum iodate in aqueous magnesium chloride solutions

MOLALITY OF ADDED SALT	SOLUBILITY OF $\text{La}(\text{IO}_3)_3$ (BY ANALYSIS)	DENSITY AT 25°C. (EXPTL.)	SOLUBILITY OF $\text{La}(\text{IO}_3)_3$ (CALCULATED)	μ MOLAL	$\mu^{\frac{1}{3}}$	$\log \frac{S}{S_0}$	$-\log \gamma_{\pm}$	γ_{\pm}
	moles per liter		moles per 1000 g.					
0.0000	0.0006634	0.99749	0.0006653	0.003992	0.06318		0.0953	0.8030
							0.09555	0.8025
0.0010	0.000702	0.99757	0.000704	0.007226	0.08503	0.02478	0.12033	0.7580
0.005	0.000817	0.99798	0.000820	0.019919	0.14113	0.09072	0.18627	0.6512
0.010	0.000908	0.99841	0.000911	0.035466	0.18833	0.13634	0.23189	0.5863
0.050	0.001306	1.00180	0.001311	0.157866	0.39732	0.29466	0.30021	0.4072
0.100	0.001601	1.00589	0.001608	0.309648	0.55645	0.38338	0.47893	0.3319
0.500	0.002782	1.03666	0.002817	1.516902	1.2316	0.62669	0.72224	0.1896
1.000	0.003508	1.07255	0.003590	3.021540	1.7382	0.73200	0.82755	0.1487
2.000	0.004209	1.13805	0.004413	6.026478	2.4549	0.82171	0.91726	0.1210
3.000	0.004639	1.19716	0.004995	9.029970	3.0050	0.87550	0.97105	0.1069

Note: Each of the values given above is the mean of the results from at least two experiments.

In figure 1 the molal solubilities of lanthanum iodate in each of the four solvents are plotted against the cube root of the molality of solvent salt. The cube root plot was resorted to in order that the points representing low concentrations would be spread more evenly upon the curve. It is

believed that the inflection points observed at high concentrations in the sulfate curves have no especial significance and are occasioned only by the

TABLE 4

The solubilities and activity coefficients of lanthanum iodate in aqueous magnesium sulfate solutions

MOLALITY OF ADDED SALT	SOLUBILITY OF $\text{La}(\text{IO}_3)_3$ (BY ANALYSIS)	DENSITY AT 25°C. (EXPTL.)	SOLUBILITY OF $\text{La}(\text{IO}_3)_3$ (CALCULATED)	μ MOLAL	$\mu^{\frac{1}{2}}$	$\log \frac{S}{S_0}$	$-\log \gamma_{\pm}$	γ_{\pm}
	moles per liter		moles per 1000 g.					
0.0000	0.0006634	0.99749	0.0006653	0.003992	0.06318		0.09555	0.8025
0.0010	0.000846	0.99766	0.000848	0.009088	0.09533	0.10551	0.20106	0.6294
0.005	0.001209	0.99839	0.001213	0.027278	0.16497	0.26078	0.35633	0.4402
0.010	0.001448	0.99921	0.001452	0.048712	0.22071	0.33899	0.43454	0.3677
0.050	0.002384	1.00496	0.002390	0.214310	0.46293	0.55540	0.65095	0.2234
0.100	0.003021	1.01167	0.003028	0.418168	0.64665	0.65813	0.75368	0.1763
0.500	0.005863	1.06116	0.005879	2.035274	1.4266	0.94627	1.04182	0.0908
1.000	0.008198	1.12180	0.008227	4.049362	2.0123	1.09222	1.18777	0.0649
1.500	0.009690	1.17865	0.009759	6.058554	2.4614	1.16635	1.26190	0.0547
2.000	0.010558	1.23098	0.010702	8.064212	2.8397	1.20644	1.30199	0.0499

Note: Each of the values given above is the mean of the results from at least two experiments.

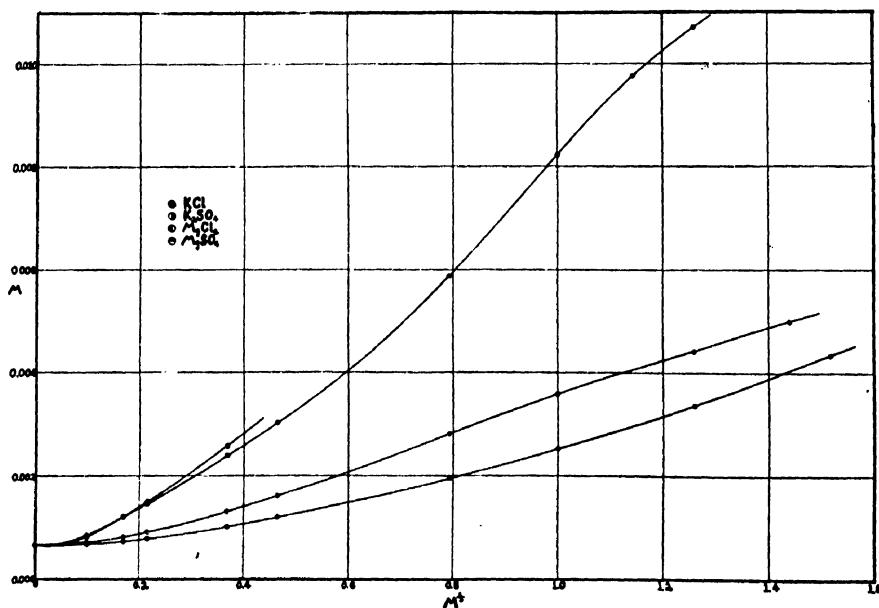


Fig. 1. Plot of molal solubilities of lanthanum iodate in salt solutions against the cube root of the molality of the solvent salt.

method of plotting. Simple solubility versus molality curves do not exhibit these inflection points.

The relative positions of the curves are important. It will be noticed that lanthanum iodate is least soluble in potassium chloride, slightly more soluble in magnesium chloride, much more soluble in magnesium sulfate, and most soluble in potassium sulfate solutions. The high solubility observed in the sulfate solutions is accounted for in the section on theory. The relative positions of the magnesium and potassium salt curves are more difficult to explain. In the section on theory it was postulated that the solubility behavior of salts depends upon the antagonistic action of two forces. One of these is the salting-out effect due to hydration. The other is the salting-in effect due to a shift in the composition of the ion atmosphere. Two chloride ions, as in magnesium chloride, should have a greater effect in increasing the solubility than the single chloride ion of potassium chloride. This is true in spite of evidence that the magnesium ion has a greater salting-out effect than the potassium ion². The solubility should therefore be greater in magnesium chloride than in potassium chloride solutions, which agrees with experiment.

If the salting-out tendency of one magnesium and two potassium ions were the same, we should expect lanthanum iodate to have the same solubility in the two chloride salts of these elements at the same chloride-ion activity. It is actually found that the solubility in 1 *M* magnesium chloride is only 4 per cent less than that in 2 *M* potassium chloride, so that this expectation is almost realized.

Conversely, where we have two salts which have the same anion, the salting-in effect upon a saturating salt with a high valence cation will be practically the same. The greater hydrating power and salting-out tendency of the magnesium ion over that of even two potassium ions reduces the solubility of the saturating salt in magnesium sulfate to below that in potassium sulfate solution.

ACTIVITY COEFFICIENTS

Referring again to the tables, in the seventh columns are found the common logarithms of the solubility ratios. The solubility ratio is the molal solubility of the lanthanum iodate in the salt solutions divided by the molal solubility in pure water. It gives the relative increase in solubility produced by the addition of the solvent salt. In the final two

² While authorities differ on the exact values of the effective radii of ions, all agree that the magnesium ion is much smaller than the potassium ion. Eldridge (*The Physical Basis of Things*, p. 247. McGraw-Hill Book Co., New York (1934)), states that if the ion is considered as a charged sphere, its potential is proportional to the charge, and inversely proportional to the radius. A small ion will therefore have a greater charge density than a large ion of the same valence. The charge density of an ion will determine its extent of hydration, and hence its salting-out effect. See also Clark: *The Electronic Structure and Properties of Matter*, John Wiley and Sons, New York (1934).

columns are found the negative logarithms of the mean molal activity coefficients, and the mean molal activity coefficients of the lanthanum and iodate ions as defined by Lewis and Randall (11).

Experimentally, the mean molal activity coefficient, γ_{\pm} , is obtained from the relation,

$$\frac{S_0}{S} = \frac{\gamma_{\pm}}{\gamma_{\pm 0}}$$

from which, by taking the common logarithm of both sides, we obtain the expression:

$$-\log_{10} \gamma_{\pm} = \log_{10} \frac{S}{S_0} - \log_{10} \gamma_{\pm 0}$$

The constant value, $-\log \gamma_{\pm 0}$, is the logarithm of the mean activity coefficient of the saturating salt ions in the pure solvent and can be obtained in several ways. Two independent methods were used in the present investigation. The first method involved the plotting of the values of $\log \frac{S}{S_0}$ at low concentrations against $\sqrt{\mu}$ on a large scale and extrapolating the curve to zero ionic strength. A series of extrapolations was carried out independently by six different persons on the potassium chloride and magnesium chloride curves. A mean of all readings on the two curves gave a value of $-\log_{10} \gamma_0 = 0.0953$. The second method involved the calculation of $-\log_{10} \gamma_0$ from the Debye-Hückel limiting law (4):

$$-\log_{10} \gamma_{\pm 0} = -\frac{1.814 \times 10^6}{(D_0 T)^{3/2}} \cdot Z_1 Z_2 \sqrt{\mu_0}$$

Here Z_1 and Z_2 are the valences (3, -1) of the ions of the saturating salt; $D_0 = 78.77$, Drude's value of the dielectric constant of water at $T = 298.1^\circ\text{A}$. Calculated from this expression $-\log_{10} \gamma_{\pm 0} = 0.0955$, which is in excellent agreement with the experimental value.

Figure 2 shows the values of $\log \frac{S}{S_0}$ plotted against the values of the square root of the total ionic strength of the solution. If the linear relation above holds, this plot should give a straight line. The line corresponding to the limiting law given above is also shown. The curves for lanthanum iodate in potassium chloride and magnesium chloride solutions fuse into that of the limiting law at low concentrations. Those for the salt in potassium sulfate and magnesium sulfate solutions show the characteristic "hump", or positive deviation from the limiting law observed by other investigators (2, 7, 9, 10, 12). Instead of fusing into the limiting law line at low concentrations, these curves cross the line at an ionic strength of about 0.0056 and finally join each other if continued a short distance below the axis.

The relative positions and shapes of the curves resulting from the present investigation are in agreement with the work of Brönsted and La Mer (1), La Mer, King, and Mason (9), and La Mer and Mason (10), using cobaltammines as saturating salts, and with that of La Mer and Goldman (7) using lanthanum iodate. The results of Peterson and Meyers (12) are not entirely confirmed in that, while they find similar curves for copper iodate in potassium sulfate and potassium chloride solvents, their curves for this salt in *both* magnesium sulfate and magnesium chloride solutions fall below that for the salt in potassium chloride. This behavior of their magnesium sulfate curve cannot be explained on the

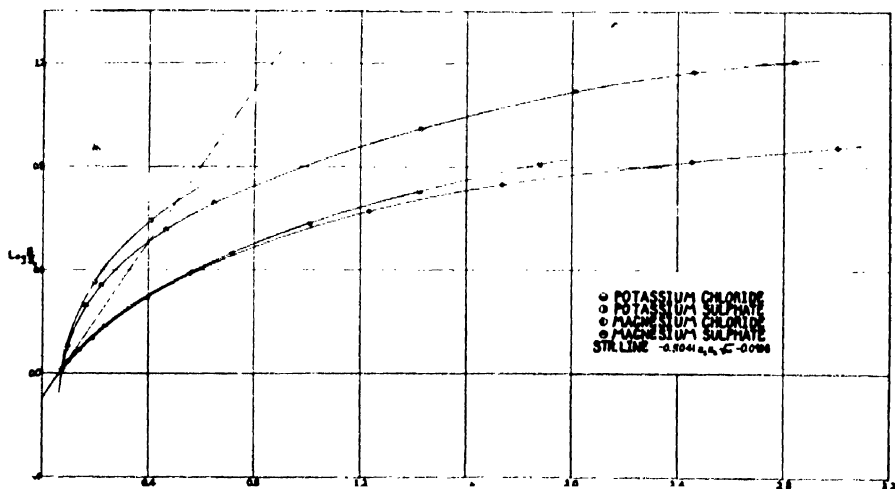


FIG. 2. Values of $\log \frac{S}{S_0}$ plotted against the values of the square root of the total ionic strength of the solution.

basis of the theory postulated (see page 97), even though copper iodate has a lower valence cation and would hence be less affected by shifts in the ion atmosphere.

Numerous attempts have been made to develop mathematical relations in harmony with the experimental behavior of saturating salts of unsymmetrical valence type in ion solvents. Up to the present time most of these have been only partially successful. It is probable that the Debye-Hückel extension of La Mer, Gronwall, and Greiff (8) comes as near as any to a satisfactory solution.

SUMMARY

The solubility behavior of lanthanum iodate at 25°C. has been investigated in solutions of potassium chloride, potassium sulfate, magnesium

chloride, and magnesium sulfate from 0.001 molal up to concentrations approaching saturation.

The solubility of lanthanum iodate is increased by the presence of added salts. The effect of the different salt types is in the order $\text{KCl} < \text{MgCl}_2 < < < \text{MgSO}_4 < \text{K}_2\text{SO}_4$, which agrees with the work of earlier investigators.

A modern theory of solubility has been postulated to explain the effects observed.

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THE CATALYTIC ACTIVITY OF COBALT MIXED WITH CERTAIN METALS FOR THE GAS-PHASE REDUCTION OF NITROBENZENE TO ANILINE¹

F. A. GRIFFITTS AND O. W. BROWN

Laboratory of Physical Chemistry, Indiana University, Bloomington, Indiana

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Many data are available which prove clearly that cobalt is an excellent catalyst for complete hydrogenations. The present experiments have been made in an endeavor to prepare an active cobalt catalyst capable of effecting partial rather than complete hydrogenations. The activity of the various catalyst preparations was judged by the completeness with which nitrobenzene could be converted into aniline.

EXPERIMENTAL METHODS AND RESULTS

The apparatus used, the technique employed to control all factors of the experiment, the method of purification of materials, and the analysis of the products have been described in a previous paper (1).

Catalyst A. A pure cobalt catalyst

Twenty-seven and five-tenths grams of c. p. cobalt nitrate hexahydrate was dissolved in 300 ml. of water and added to a solution of sodium hydroxide containing 8.35 g. of sodium hydroxide. The precipitated hydroxide was collected on a filter, thoroughly washed, dried at 105°C. for twenty-four hours, and ignited in a muffle furnace for one hour at 280°C. to remove "bound water". The latter temperature was measured by a thermometer. The data secured over this catalyst are in table 1.

Catalyst B. A pure cobalt catalyst supported on asbestos

This catalyst was prepared exactly as catalyst A, except that before mixing the solutions the asbestos was thoroughly saturated with sodium hydroxide. The data for the catalyst are shown in table 2. This yield shows that the yield of a supported catalyst is comparable to one non-supported.

¹ Presented before the Division of Inorganic and Physical Chemistry at the Ninety-third Meeting of the American Chemical Society, Chapel Hill, North Carolina, April 14, 1937.

Catalyst C. A cobalt-manganese catalyst

The preparation followed the plan given by M. Salinger (3) for making cobalt permanganate by use of cobalt nitrate, potassium permanganate, and an excess of hydrogen peroxide in the presence of some sodium carbonate to reduce acidity. The material was dried at 105°C. for twenty-four hours and ignited in the muffle furnace for two hours at 285°C. This catalyst was divided into two batches as C1 and C2. Data from this

TABLE 1

The effect of temperature on the activity of a pure cobalt catalyst

Weight of catalyst A, 6.5 g.; temperature of reduction, 215°C.; rate of flow of hydrogen, 10 liters per hour; rate of flow of nitrobenzene, 2.3745 g. per hour

TEMPERATURE	YIELD OF ANILINE IN PER CENT OF THEORY
°C.	per cent
215	36.2*
260	5.0
250	
243	24.4
243	27.7†
235	32.2†

* All figures represent rough averages, since excellent checks for low yields are not common.

† The nitrobenzene rate was 4.7509 g. per hour.

TABLE 2

The activity of a cobalt catalyst supported on asbestos

Weight of catalyst B, 5.5 g., including the support; temperature of reduction of oxide, 252°C.; rate of flow of hydrogen, 10 liters per hour; rate of nitrobenzene flow, 4.7508 g. per hour

TEMPERATURE	YIELD OF ANILINE IN PER CENT OF THEORY
°C.	per cent
252	8.05

catalyst are in table 3, one case showing the effect of making the second temperature used higher than the first and the other showing the effect of making the second temperature lower than the first.

These data show the great sensitivity of cobalt-bearing catalysts to small temperature changes. The usual rule seems to be that after a catalyst has operated at a lower temperature it will suffer a severe hysteresis effect, so that it will not give good yields later. Notice the effect of operating at 223°C. in the case of catalyst C1.

Catalyst D. A cobalt-manganese catalyst prepared like catalyst C and supported on purified asbestos

The data with this catalyst were taken over a wide range of temperatures, all of which gave reasonably good yields except one at 235°C. (See table 4.) All of the factors, exclusive of temperature, were the same as those given in table 3. Attention should be given to the fact that, for

TABLE 3

The effect of temperature on the aniline yield over a cobalt-manganese catalyst
Temperature of reduction, 260°C.; weight of catalyst C1 and C2, 5.25 g.; rate of flow of nitrobenzene, 2.3754 g. per hour; rate of flow of hydrogen, 10 liters per hour

CATALYST	TEMPERATURE	YIELD OF ANILINE IN PER CENT OF THEORY
	°C.	per cent
C1.....	260	86.9
	223	36.0
	250	54.8
	272	44.5
	290	16.2
	325	
C2.....	260	99.2
	268	93.6
	255	88.8
	262	87.0

TABLE 4

The effect of temperature on the aniline yield over catalyst D

TEMPERATURE	YIELD OF ANILINE IN PER CENT OF THEORY	TEMPERATURE	YIELD OF ANILINE IN PER CENT OF THEORY
°C.	per cent	°C.	per cent
260	55.6	270	78.9
250	70.3	288	77.4
245	86.9	255	85.7
242	88.2	252	73.3
235	16.2	265	72.8
268	93.4	270	73.3

some reason that is not yet known, a good yield was obtained at 268°C. following the trial at 235°C.

Catalyst E. A cobalt-molybdenum catalyst

The catalyst used in this case was secured by means of cobalt molybdate made by the method given by Markwald (2). Equivalent quantities of cobalt nitrate and sodium molybdate were mixed in solution. The purple

to lavender colored precipitate was collected, filtered, washed, dried twenty-four hours at 105°C., and heated in a muffle furnace for two hours at 330°C. Data are shown in table 5. The outstanding feature of these data indicates that such a combination has to operate at a temperature higher than that of most such catalysts.

TABLE 5

To show the nature of a mixed cobalt-molybdenum catalyst

Weight of catalyst E, 7 g.; catalyst reduced at 255°C., oxidized with air, and reduced again at 260°C.; rate of flow of hydrogen, 10 liters per hour; rate of flow of nitrobenzene, 4.7509 g. per hour

TEMPERATURE	YIELD OF ANILINE IN PER CENT OF THEORY
°C.	per cent
260	
290	7.6
312	23.1
320	89.3
332	85.4
310	82.9

TABLE 6

Summary for cobalt-chromium catalysts

COMPOSITION IN MOLE PER CENT OF COBALT AND CHROMIUM	TEMPER- ATURE OF IGNI- TION	TEMPER- ATURE OF REDUC- TION	WEIGHT OF CATA- LYST	RATE OF FLOW OF HYDRO- GEN	RATE OF FLOW OF NITRO- BENZENE	TEMPER- ATURE OF OPERA- TION	PER CENT YIELD OF ANILINE
	°C.	°C.	grams	liters per hour	grams per hour	°C.	per cent
50:50	300	260	6	10	4.7508	270	89.4
						280	64.3
98:2	320	262	8	10	4.7508	264	74.4
						281	79.0
98.5:1.5	310	265	7	10	4.7508	280	63.4 (average of several)
99.0:1.0	300	265	6.5	10	4.7508	265	25.0 (average)

Catalyst F. Cobalt-chromium mixtures

Three cobalt-chromium bearing catalysts were prepared from solutions of cobalt nitrate and sodium chromate. They were prepared so that they contained cobalt and chromium in the following molecular ratios: 50:50, 98:2, 98.5:1.5, and 99:1. The general treatments of washing, drying, etc. were similar to those previously given. A summary of results is shown in table 6. In many ways these data are interesting and instructive. In the first place it appears possible that an optimum composition might be found that would be an excellent catalyst. It is also

to be noted that the used catalyst is green, indicating oxidation to an oxide. Furthermore the catalyst seems to get less effective on successive runs. Finally, the results over these chromium-containing catalysts present a contrast with certain others that contain chromium, e.g., those used in methanol production. Excellent hydrogenation is secured by the latter, whereas the cobalt-chromium oxide catalysts tried were not satisfactory for the reduction to aniline.

SUMMARY

1. Cobalt is too active to hydrogenate nitrobenzene to aniline.
2. A cobalt-manganese mixture, while very sensitive to temperature, will give excellent aniline yields.
3. Cobalt molybdate, operating at a much higher temperature, is fairly efficient.
4. Various proportions of cobalt and chromium were studied, none of which was an excellent catalyst.

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THE RATE OF REACTION OF AMALGAMS WITH ACIDS. I

LITHIUM AMALGAMS¹

FRANK A. FLETCHER AND MARTIN KILPATRICK

Laboratory of Physical Chemistry, University of Pennsylvania, Philadelphia, Pennsylvania

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In a study of the rate of solution of magnesium in acids (4) evidence for the general kinetic equation for this reaction

$$v = k_1C_{H_2O} + k_2C_{H_3O^+} + k_3C_A \dots \dots \text{etc.} \quad (1)$$

where A represents an acid other than hydrogen ion (H_3O^+) was presented. Whether the measured rates are controlled by diffusion or by the chemical process the logical interpretation of the results is from the point of view of the extended theory of acids. Preliminary experiments with alkali metal amalgams (3) partially confirmed equation 1, and the work of Brönsted and Kane (1) with dilute sodium amalgams offered evidence that the dissolution of sodium amalgam is due to the reaction of the metal with the acid molecule. Brönsted and Kane worked with dilute amalgams and an excess of weak acid. They found that sodium as amalgam dissolved with a velocity which was directly proportional to the square root of the sodium concentration in the amalgam.

Most of the work described in the literature has been concerned with sodium or potassium amalgams. Lithium amalgam was chosen in the hope that the study could be extended to non-aqueous solutions.

EXPERIMENTAL PROCEDURE

A. Preparation of amalgams

The lithium amalgams used in this work were prepared by the electrolysis of lithium hydroxide solutions, using a platinum anode and a mercury cathode.

All mercury used was purified by running it five times through a four-foot column of dilute nitric acid. In the first part of the work the mercury

¹This article is abstracted from the dissertation of Frank A. Fletcher, which was presented to the Faculty of the Graduate School of the University of Pennsylvania in partial fulfillment of the requirements for the degree of Doctor of Philosophy, December 1, 1935.

was next treated by the method of Brummer and St. von Náray-Szabó (2), which consisted in oxidizing the impurities in the mercury anodically in a slowly rotating anode. This anode is dipped into a solution of mercurous nitrate and nitric acid. The cathode consists of mercury. The next step in the purification was the washing, drying, and distillation of the metal under vacuum. It was found unnecessary to use the method of Brummer and St. von Náray-Szabó, and consequently that part of the procedure was omitted. No difference was noted between amalgams made with the mercury treated by their method and then distilled and those made with mercury which was distilled only.

The amalgam, itself, was prepared by the electrolysis of lithium hydroxide solution, using a platinum anode and a mercury cathode. The apparatus consisted of four main parts: the electrolysis chamber, A; the drying chamber, H; the filtration system, L; and the receiver, M.

The electrolysis chamber consisted of a glass tube, 4 cm. inside diameter and 21 cm. long. One end was closed by a large rubber stopper (with holes for electrodes and stirrer), and the other end by a stopcock B. The cathode leads C consisted of copper wires soldered to platinum wires, which were sealed into glass tubing making connection with the mercury D. The anode, E, consisted of a piece of platinum sheet 2.5 cm. by 2.5 cm. The stirrer, F, consisted of a small glass rod immersed in the mercury and used for stirring the amalgam.

After filling the electrolysis chamber about half full of mercury, the two sealed electrodes were immersed, the chamber was filled with approximately 5 molar lithium hydroxide solution, and the electrical circuit was connected. Current was passed through the solution until the amalgam was judged to be of the proper strength (not greater than about 1 molar to remain fluid).

During the electrolysis a large amount of oxygen was evolved at the anode and a considerable amount of hydrogen was evolved at the mercury surface. It was found necessary to stir the mercury occasionally to distribute the amalgam. There was a tendency to crust formation on the mercury surface, which is presumably due to formation of some solid amalgam. After the electrolysis about one-half of the amalgam was run into some previously purified mercury already in the drying chamber.

The drying chamber, H, consisted of a tube 4 cm. in diameter and 12 cm. long. It was closed at both ends by stopcocks, G and B. A capillary T-tube was sealed to the drying chamber at K. This T-tube had two stopcocks sealed to it for admission of nitrogen and for connection to the vacuum line. The advantage of dropping the amalgam into mercury was (1) that it helped to cool the amalgam, and (2) that it helped to dilute the amalgam. Since the current efficiency of the electrolysis could not be known with accuracy, it was largely a matter of experience to determine the length of time needed to prepare a batch of amalgam. If the elec-

trolysis was continued for too long a time, the amalgam would turn pasty on cooling in the drying chamber, unless it was mixed with fresh mercury. Before being used, the drying chamber was carefully cleaned, dried, and filled with dry nitrogen gas. As soon as all of the amalgam had been run into the drying chamber, the vacuum line was attached to the proper stopcock and small amounts of moisture sucked out.

After drying, the amalgam was admitted to the filtration chamber, L, which consisted of a small Jena tube containing a sintered glass plate.

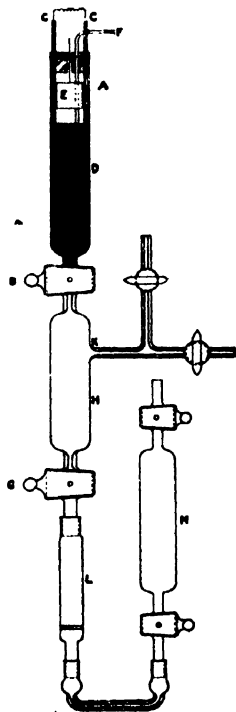


FIG. 1

FIG. 1. Apparatus for preparing amalgam

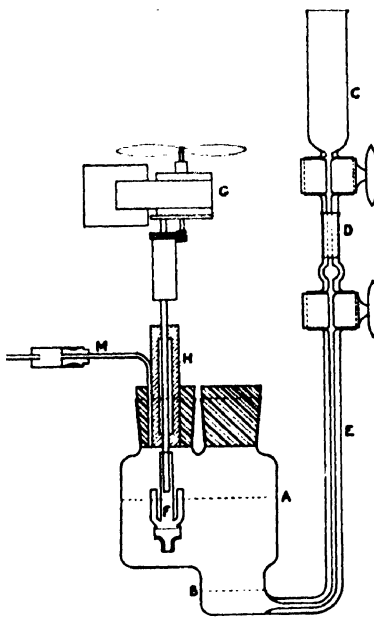


FIG. 2

FIG. 2. Reaction vessel

The tube was attached to the drying chamber by means of a ground-glass joint, and to the U-tube below it by similar means.

This U-tube was joined to a 125-cc. Pyrex gas pipet by means of a third ground-glass joint. The end of the pipet, M, was ground to fit the joint in this apparatus. A joint in a similar U-tube (with a stopcock at one end) was used for transferring the amalgam from the reservoir to the funnel in the reaction vessel as needed.

When a vacuum was applied at the top of the pipet, the amalgam was sucked out through the filtering chamber, through the U-tube into the gas pipet. If the amalgam was too concentrated in any case, crystals collected on the filter plate and filtration ceased.

B. Reaction apparatus

The reaction apparatus consisted of a solution chamber, A, of about 250-cc. capacity, sealed to an amalgam chamber, B, of about 20-cc. capacity. Amalgam was delivered to the amalgam chamber by the funnel, C, through the ground-glass joint, D, and capillary tube, E, approximately 15 cm. long. The solution was stirred by means of a stirrer, F, operated in most of the experiments by a synchronous motor, G, through a mercury-sealed shaft, H, of the type shown in detail by Kilpatrick and Rushton (4). The hydrogen was conducted from the apparatus by means of tube M to the gas collection apparatus, consisting of two 100-cc. water-jacketed gas burets and a leveling tube.

In a study of the water reaction of lithium amalgam the hydrogen was not collected. An indicator was added to the water and acid added from a microburet as fast as lithium hydroxide was formed in solution, as described by Kilpatrick and Rushton (4).

C. Details of procedure

Experiments for the measurement of the acid reaction rate constant were carried out as follows: A known volume (usually 150 cc.) of acid or buffer was added by pipet to the reaction apparatus. Dry nitrogen gas was bubbled through the apparatus to remove oxygen partially. Then the gas collection apparatus was connected to the system, amalgam run from the funnel, C, into the amalgam reservoir, B, the synchronous motor started, and the gas measurements made each minute. The gas temperature was taken as that of the water in the jacket about the gas burets. The barometric pressure was noted. After the reaction was completed, the solution in the reaction vessel was analyzed for acidic or basic content, and the mercury was weighed. By calculating the volume of hydrogen equivalent to the acid used, and subtracting from this the individual readings, a series of figures was obtained which were proportional to the acid concentration. If the logarithm of this series was plotted against time and the slope of the resultant line calculated, it was possible to determine the reaction rate constant for the acid in question.

In the case of the water reactions, the procedure was somewhat similar. The quantity of standard acid added at any time was equivalent to the lithium in the amalgam which reacted. The concentration of the lithium in the amalgam was then equivalent to the difference between the original lithium in the amalgam and the lithium that had reacted. Following Brönsted and Kane, we found that the rate constant could be calculated from the square-root equation. A synchronous motor was used only in the acid rate experiments. A direct current, rheostat-controlled motor was used in the water reaction experiments. The speed was kept as constant as possible by observing a tachometer connected to the motor and adjusting the rheostat accordingly.

EXPERIMENTAL RESULTS

Hydrochloric acid reactions

Hydrochloric acid solutions were used in the measurement of the reaction rate of H_3O^+ with lithium amalgam. In such a reaction the rate is equal to that of the water reaction plus that for the H_3O^+ reaction, since both processes go on simultaneously. In experiments with acids it was necessary to operate within a narrow concentration range to avoid, first, the experimental difficulty of too fast a reaction if the acid concentration chosen was too high (above 0.045 *M*), and second, the difficulty of determining the reaction velocity constant from the data if the acid concentration chosen was too low (less than 0.015 *M*), owing to the fact that the water reaction rate became an appreciable portion of the whole rate, and owing to the presence of an induction period. The equation used to calculate the velocity constant of the acid reactions is:

$$k = \frac{2.303 V}{St} \log \frac{a}{a-x} \quad (2)$$

where *k* is the reaction velocity constant, *V* is the volume of acid solution in cm.³, *S* is the area of the mercury surface in cm.², *t* is the time in minutes, *a* is the initial acid concentration in moles per liter, and (*a* - *x*) is the acid concentration at time *t*. The units for *k* in the above equation are cm. × minutes⁻¹. All values of *k* for hydrochloric acid, perchloric acid, formic acid, cyanoacetic acid, and acetic acid reactions are so expressed. If log (*a* - *x*) is plotted against the time, the slope of the line is equal to $-\frac{kS}{2.303V}$.

Table 1 gives the results with the hydrochloric and perchloric acids. From this table it is evident that the rate of reaction is independent of the concentration of the lithium in mercury and proportional to the acid concentration. The slightly higher values of the velocity constant at higher concentration may be attributed to the higher concentration of salt in the aqueous solution. The velocity constants for the perchloric acid solutions are somewhat less than those for the hydrochloric acid. An unusually high velocity constant was found in two experiments. Both of these results were obtained after cleaning the apparatus with hot chromic acid. This treatment was followed by rinsing ten times with water. One explanation is that chromic acid or some component of the cleaning solution is strongly absorbed on the glass surface and that the presence of this material or an activation at the glass-mercury interface causes a more rapid reaction.

The effect of temperature on the rate of reaction is given in table 2. The effect of temperature is small.

The effect of stirring is shown in table 3. The effect of stirring at a liquid-liquid interface when the reaction is followed by gas evolution is a

TABLE 1

Reaction of lithium amalgam with the acid H_2O^+

Surface, 9.63 cm.²; R.P.M., 975; volume, 150 cc.; temperature, 25°C.

ACID	INITIAL CONCENTRA- TION OF ACID	INITIAL CONCENTRA- TION OF AMALGAM	VELOCITY CONSTANT <i>k</i>	REMARKS
	<i>moles per liter</i>	<i>moles per liter</i>		
HCl	0.0195	0.39	1.09	Average of 2 experiments
	0.0249	0.39	1.07	Average of 7 experiments
	0.0327	0.39	0.98	Average of 4 experiments
	0.0326	0.68	1.24	Average of 2 experiments
	0.0332	0.41	1.06	0.10 M LiCl
HClO ₄	0.0240	0.41	0.97	Average of 4 experiments
	0.0355	0.41	0.90	Average of 2 experiments
	0.0340	0.77	1.14	0.26 M LiClO ₄
	0.0444	0.77	1.04	
	0.0444	0.41	0.94	Average of 3 experiments

TABLE 2

*Variation of *k* with temperature*

Surface, 9.63 cm.²; R.P.M., 975; volume, 150 cc.

TEMPERATURE	HYDROCHLORIC ACID	AMALGAM	<i>k</i>	REMARKS
°C.	<i>moles per liter</i>	<i>moles per liter</i>		
20	0.0249	0.39	0.90	Average of 2 experiments
25	0.0249	0.39	1.07	Average of 7 experiments
30	0.253	0.39	1.30	Average of 3 experiments

TABLE 3

Effect of stirring speed on velocity constant

Surface, 9.63 cm.²; volume, 150 cc.; temperature, 25°C.

R. P. M.	HYDROCHLORIC ACID	AMALGAM	<i>k</i>
	<i>moles per liter</i>		
520	0.0253	0.39	0.89
975	0.0249	0.39	1.07
2450	0.0253	0.39	2.10

difficult problem. In the first place the aqueous solution must be sufficiently agitated to prevent supersaturation in that phase. On the other hand, the stirring should not change the surface at the interface. In

addition, the stirring is dependent on the shape of the vessel and the position of the stirrer.

Reactions with weak acids

For this portion of our study we used acetic acid, formic acid, cyanoacetic acid, and *o*-chlorophenol. Buffer solutions prepared from stock solutions of lithium hydroxide and the acid were used. It will be shown in the next section that the presence of sodium or potassium salt in the buffer solution introduces that element into the amalgam in place of some of the lithium. This seems to have been overlooked by others (1). In all cases preliminary experiments were carried out to see that the volume of gas evolved corresponded to the amount of lithium that reacted. The amount of metal that reacted was calculated from the weight of the amalgam taken and the analysis of the amalgam. We were not able to use a buffer of chloroacetic acid, since either the acid or its anion was reduced. In the case of all weak acids except the *o*-chlorophenol the experimental procedure and method of calculation of the velocity constants were the same as for the experiments with the strong acids.

On examination of table 4 it will be noted that the concentration range is rather limited. This is due to the fact that the reaction is too rapid to measure above the initial concentration indicated, if lithium amalgam is used.

The velocity constants are practically the same in the cases of the three acids used. It is evident that diffusion in the aqueous solution may be the controlling process. Since we have reduced the hydrogen-ion concentration to a very low value, the important diffusion processes in the aqueous solution are the diffusion of the acid molecule to the interface and the movement of the reaction products from the surface.

Experiments with o-chlorophenol

In this case we found that the rate was proportional to the square root of the lithium concentration in the amalgam. The rate constants were calculated from the equation:

$$Sk = \frac{2(\sqrt{C_m^0} - \sqrt{C_m})}{t} \quad (3)$$

where C_m^0 and C_m are the molar concentrations of the lithium in the amalgam at the beginning of the reaction and at time t , respectively. Time is expressed in minutes. No reduction of the *o*-chlorophenol was found.

The velocity constant k also includes the water reaction. It is, however, about three or four times greater than the constant for the water reaction, which, as shown in the next section, also follows the square-root law. Our

TABLE 4

*Reaction of lithium amalgam with weak acids*Surface, 9.63 cm.²; R.P.M., 975; volume, 150 cc.; temperature, 25°C.; initial amalgam concentration, 0.41 molar

ACID	INITIAL CONCENTRATION OF ACID	INITIAL ANION CONCENTRATION	<i>k</i>
	<i>moles per liter</i>	<i>moles per liter</i>	
Acetic acid.....	0.0657	0.0657	0.575
	0.0473	0.0473	0.517
	0.0394	0.0394	0.508
	0.0394*	0.0400	0.488
	0.0329	0.0329	0.575
	0.0295†	0.0300	0.550
	0.0262	0.0262	0.473
			Av. = 0.523
Formic acid.....	0.0488	0.0488	0.565
	0.0390	0.0390	0.557
	0.0325	0.0325	0.545
	0.0325	0.0325	0.560
	0.0293	0.0293	0.564
			Av. = 0.558
Cyanoacetic acid.....	0.0305	0.0953	0.540
	0.0305	0.0953	0.541
	0.0305	0.0953	0.547
	0.0305	0.0953	0.549
	0.0305	0.0953	0.549
	0.0283	0.0953	0.630
	0.0283	0.0953	0.616
			Av. = 0.567

* Also 0.01 molar in LiCl.

† Also 0.02 molar in LiCl.

TABLE 5

*Experiments with o-chlorophenol*Surface, 9.63 cm.²; R.P.M., 975; volume, 150 cc.; temperature, 25°C.; initial amalgam concentration, 0.41 molar

INITIAL CONCENTRATION OF ACID	INITIAL ANION CONCENTRATION	<i>k</i> × 10 ³
<i>moles per liter</i>	<i>moles per liter</i>	
0.1164	0.1	4.14
0.145	0.1	5.14
0.1129	0.1	4.42
0.1129	0.1	4.43
0.1129	0.1	4.54
Average.....		4.53

results indicate that for stronger acids the reaction follows the monomolecular law and that for very weak acids and water the square-root law is obeyed. It may be that between these two limits there will be some acid where a combination of the two laws must be taken into account.

The water reaction

Equation 1 contains a term to take the water reaction into account. In order to determine the order of magnitude of this reaction, we carried out a large number of experiments involving the rate of reaction of lithium amalgam with water and with certain salt solutions.

The procedure was as follows: Water (or salt solution) and an indicator were added to the reaction vessel. A 5-cc. microburet, containing standard hydrochloric acid, was arranged over the vessel, and amalgam was admitted. The vessel was open to the air. As the reaction took place, the standard acid was added at a rate great enough to keep the hydrogen-ion

TABLE 6
Effect of hydrogen-ion concentration
R.P.M. = 900

	HYDROGEN-ION CONCENTRATION	$k_w \times 10^3$
	<i>moles per liter</i>	
Thymol blue.....	4×10^{-10}	0.54
Phenolphthalein.....	1×10^{-9}	0.93
Bromothymol blue.....	1×10^{-7}	0.89
Methyl red.....	1×10^{-6}	1.36
Bromocresol green.....	2×10^{-6}	0.69
Bromophenol blue.....	1×10^{-4}	1.27

concentration approximately constant. Time and buret readings were recorded. This is the method used by Kilpatrick and Rushton (4).

Our results, given in table 6, confirm the results of Brönsted and Kane (1) that the rate of dissolution of an amalgam is proportional to the square root of the amalgam concentration. All of the above values of k were calculated by equation 3. The concentration units are moles per liter and the time unit is the minute. All constants are based on an interfacial area of 1 cm.²

The results indicate that the velocity constant is independent of the hydrogen-ion concentration between 1×10^{-4} and 1×10^{-10} , although the experiments are not very reproducible. The effect of temperature between 16°C. and 26°C. on these experiments was within the experimental error. The result for each indicator in the table is the average of a large number of measurements.

A number of interesting experiments were carried out using salt solutions

in place of water (see table 7). All experiments were comparable with one another. When 1 molar sodium chloride was used the rate constant was much closer to that of sodium amalgam reacting with water than that of lithium amalgam. With lithium amalgam and 1 molar potassium chloride the rate was below that for lithium amalgam and water. These phenomena may be explained by assuming the reaction:



TABLE 7

Reactions of lithium amalgam with aqueous salt solutions
Surface, 9.63 cm.²; volume, 150 cc.; R.P.M., 900; T, 25°C.

	MOLAR CON- CENTRATION OF SALT	MOLAR CONCENTRA- TION OF	k × 10 ³
NaCl.....	1.0	0.391	0.28
NaCl.....	2.0	0.391	0.18
NaCl.....	0.5	0.391	0.29
LiCl.....	1.0	0.391	2.81
KCl.....	1.0	0.391	0.69
NH ₄ Cl.....	1.0	0.391	1.76
MgCl ₂	0.33	0.391	4.19
NaCl.....	1.0	0.047	0.50
SrCl ₂	0.33	0.047	0.33
BaCl ₂	0.33	0.047	0.34
KCl.....	1.0	0.047	0.42
CaCl ₂	0.33	0.047	1.04
MgCl ₂	0.33	0.047	1.65
CaCl ₂	1.0	0.0235	1.19
BaCl ₂	0.33	0.0235	0.75
SrCl ₂	0.33	0.0235	0.56
KCl.....	1.0	0.0235	0.66
CaCl ₂	0.33	0.0235	1.18
NaCl.....	1.0	0.0235	0.67
LiCl.....	1.0	0.0235	2.73

This reaction may not be complete, but our results indicate that it takes place to a considerable extent. It must also be a rather rapid reaction. It is of interest to know that the constant for the reaction with magnesium chloride was about twice that of the water reaction. These results are in accord with the work of Smith (7). Lewis and Macdonald also noticed the rapid displacement of lithium in the amalgam by sodium (5).

The lack of reproducibility of these experiments may be due in part to the formation of hydrogen peroxide by the reduction of oxygen. To show the effect of hydrogen peroxide on the reaction a few experiments were carried out in dilute hydrogen peroxide solutions. The results are given in table 8.

One interpretation of these results is that the reaction of lithium with water is increased by the presence of an oxidizing agent, due to the removal of a hydrogen film. If this alone were the case, an excess of hydrogen peroxide should not show such an increase in the velocity constant. This process seems to involve an additional reaction, the capture of electrons by the oxidizing agent (6). If we make the assumption that oxygen reacts with lithium amalgam with a velocity constant comparable to that attributable to hydrogen peroxide, we might expect a 10 per cent increase in the water reaction constant due to the presence of oxygen. The lack of reproducibility of the water reaction cannot be attributed to the reaction with oxygen, as experiments (1) have shown the same lack of reproducibility in cases when the oxygen concentration would certainly be small. This problem will be discussed further in a later paper.

Returning to our equation 1 and considering a reaction with (1) H_2O , (2) H_3O^+ , (3) HA , a fairly weak acid, and (4) a very weak acid, we would

TABLE 8

Effect of hydrogen peroxide on the reaction

Hydrogen-ion concentration, 1×10^{-2} ; initial amalgam concentration, 0.15; R.P.M., 1000; temperature, 25°C.

INITIAL CONCENTRATION OF H_2O_2 IN MOLES PER LITER	10^3k	$10^3(k - k_w)$ $C_{H_2O_2}$
0	0.81	
0.026	1.38	21
0.052	2.72	37
0.072	4.25	48

have for the total rate of formation of Li^+ ion in the aqueous solution, $\frac{dx}{dt}$,

in gram-ions formed per minute:

For the water reaction:

$$\frac{dx_0}{dt} = \frac{k_w \bar{V} S}{1000} \sqrt{C_m}$$

where \bar{V} is the volume of amalgam in cubic centimeters.

For the hydrogen-ion reaction:

$$\frac{dx_1}{dt} = k_1 S C_A = k_{H_3O^+} S C_{H_3O^+}$$

For HA

$$\frac{dx_2}{dt} = k_2 S C_A = k_{HA} S C_{HA}$$

For HB

$$\frac{dx_3}{dt} = \frac{\bar{V} S}{1000} k_3 C_A \sqrt{C_m} = \frac{\bar{V} S}{1000} k_{HB} C_{HB} \sqrt{C_m}$$

whence

$$\frac{dx}{dt} = \frac{d(x_0 + x_1 + x_2 + x_3)}{dt} = \frac{\bar{V}S}{1000} (k_w + k_{\text{HB}} C_{\text{HB}}) \sqrt{C_m} + S(k_{\text{H}_3\text{O}^+} C_{\text{H}_3\text{O}^+} + k_{\text{HA}} C_{\text{HA}}) \quad (4)$$

From the data

$$\begin{array}{ll} k_w = 1.19 \times 10^{-3} & k_{\text{H}_3\text{O}^+} = 1.07 \times 10^{-3} \\ k_{\text{CH}_3\text{COOH}} = 0.52 \times 10^{-3} & k_{\text{CH}_3\text{CNCOOH}} = 0.57 \times 10^{-3} \\ k_{\text{HCOOH}} = 0.56 \times 10^{-3} & \text{and } k_{o\text{-ClC}_6\text{H}_4\text{OH}} = 0.027 \end{array}$$

Computations from the above equation indicate that for reactions with the strong acids the water reaction comes in to as much as 20 per cent in some cases. In the case of cyanoacetic acid the H_3O^+ reaction comes in to approximately 10 per cent, while for the other acids the H_3O^+ reaction is negligible. In the case of *o*-chlorophenol the water reaction comes in to 30 per cent but can be directly subtracted from the overall k , as both rates are proportional to the square root of the lithium concentration. Equation 4 gives the complete equation corresponding to equation 1. The case of amalgams is considerably more complicated than that of magnesium dissolving in acids. A further discussion of the results will be given in a paper presenting the data on sodium amalgams.

SUMMARY

1. The rates of reaction of lithium amalgams with aqueous solutions of strong and weak acids have been measured.
2. A general rate equation has been derived which expresses the rate of reaction in various buffer solutions.
3. The rate of reaction of lithium amalgams with water is proportional to the square root of the lithium concentration. This rate law also applies to the reaction with *o*-chlorophenol.
4. For the other acids studied the rate is independent of the lithium concentration.
5. An explanation has been offered for the rate of reaction of amalgams with salt solutions.

Due acknowledgment is made of a grant from the Faculty Research Committee of the University of Pennsylvania to one of us (M. K.).

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THE CODEPOSITION OF METALS OF UNLIKE VALENCE IN ACID SOLUTIONS

W. GEORGE PARKS

Department of Chemistry, Rhode Island State College, Kingston, Rhode Island

AND

I. MILTON LE BARON

Department of Chemistry, Louisiana State University, Baton Rouge, Louisiana

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INTRODUCTION

The codeposition of metals in which the two metals plating were of different valence has been investigated. The following systems were included: lead-thallium, silver-copper, nickel thallium, zinc-thallium, and copper-thallium. The cathode potential method previously described (3) was employed at different current densities at room temperature, in solutions of pH 5. The variation of codeposition with the valence of the metals involved has been determined. From the data obtained a general empirical equation has been derived for such codeposition where mono- and bi-valent metals are involved. It is shown that the valence of the metals has an effect on codeposition not taken into account by the equivalent weights of the two metals plating. Glasstone (2) has made a somewhat similar study on the cathode potential of alloys of zinc, nickel, chromium, and iron. This work will be treated in a separate paper to appear shortly.

EXPERIMENTAL

The variation of the limit of codeposition with the current density was determined for the systems copper-thallium, lead-thallium, silver-copper, and nickel-thallium by the method previously described (3). The system zinc-thallium has already been reported upon (3).¹ The nitrates of the metals were used in solutions of a pH of 5 at room temperature. The data obtained are given in table 1 and are shown graphically in figures 1 to 4, inclusive.

In the figures the cathode potential is plotted against the per cent of the cation having the lower cathode potential in solution. An approximate value of the limit of codeposition may be obtained by selecting the final point of inflection in the composition-E.M.F. curve. This point may

TABLE 1
Data obtained upon codeposition of metals of unlike valence

SYSTEM	2.4 MILLIAMPS. PER CM. ²		4.4 MILLIAMPS. PER CM. ²		7.6 MILLIAMPS. PER CM. ²		10.2 MILLIAMPS. PER CM. ²	
	Cathode potential	Per cent Cu	Cathode potential	Per cent Cu	Cathode potential	Per cent Cu	Cathode potential	Per cent Cu
Thallium-copper (figure 1).....	0.656	0.00	0.671	0.00	0.698	0.00	0.714	0.00
	0.648	0.42	0.658	0.63	0.677	0.63	0.667	1.27
	0.645	0.63	0.644	0.85	0.664	0.85	0.383	1.69
	0.356	0.85	0.255	1.27	0.627	1.27	0.245	2.53
	0.039	1.06	0.055	1.69	0.238	1.69	0.200	3.40
	0.016	1.27	0.032	2.11	0.138	2.11		
	0.015	1.69	0.021	2.53	0.102	2.53		
			0.010	3.40	0.078	3.40		
SYSTEM	2 MILLIAMPS. PER CM. ²		4 MILLIAMPS. PER CM. ²		8 MILLIAMPS. PER CM. ²			
	Cathode potential	Per cent Tl	Cathode potential	Per cent Tl	Cathode potential	Per cent Tl		
Nickel-thallium (figure 2).....	0.904	0.54	0.921	0.54	0.975	0.54		
	0.861	1.09	0.910	1.09	0.952	1.09		
	0.774	1.62	0.868	1.62	0.925	1.62		
	0.755	2.17	0.847	2.17	0.885	2.17		
	0.750	2.71	0.801	2.71	0.849	2.71		
	0.747	3.20	0.780	3.20	0.825	3.20		
	0.718	7.18	0.760	4.21	0.801	3.74		
			0.745	5.43	0.771	5.01		
			0.726	7.50	0.750	6.58		
			0.722	8.60	0.745	7.18		
SYSTEM	1 MILLIAMPS. PER CM. ²		2 MILLIAMPS. PER CM. ²		3 MILLIAMPS. PER CM. ²			
	Cathode potential	Per cent Ag	Cathode potential	Per cent Ag	Cathode potential	Per cent Ag		
Copper-silver (figure 3).....	0.063	0.00	0.058	0.00	0.040	0.00		
	0.115	0.18	0.070	0.18	0.076	1.09		
	0.180	0.37	0.096	0.37	0.138	1.49		
	0.270	0.46	0.125	0.57	0.278	1.88		
	0.305	0.57	0.210	0.77	0.323	2.55		
	0.339	0.74	0.271	0.92	0.341	3.70		
	0.355	0.91	0.310	1.09				
	0.375	1.29	0.326	1.29				
	0.385	2.55	0.362	1.64				
			0.382	2.55				

TABLE 1—Concluded

SYSTEM	1.5 MILLIAMPS. PER CM. ²		2 MILLIAMPS. PER CM. ²		3 MILLIAMPS. PER CM. ²	
	Cathode potential	Per cent Pb	Cathode potential	Per cent Pb	Cathode potential	Per cent Pb
Lead-thallium (fig- ure 4).....	0.657	0.00	0.700	0.00	0.729	0.00
	0.655	0.55	0.693	1.11	0.720	1.11
	0.571	1.66	0.626	2.22	0.706	2.22
	0.485	2.77	0.535	3.32	0.680	3.32
	0.475	3.91	0.505	4.43	0.630	4.43
	0.457	11.10	0.499	5.55	0.557	5.55
			0.486	11.10	0.520	8.22
					0.513	11.10

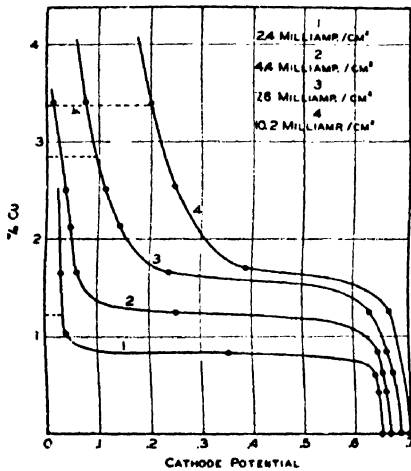


FIG. 1. The system thallium-copper

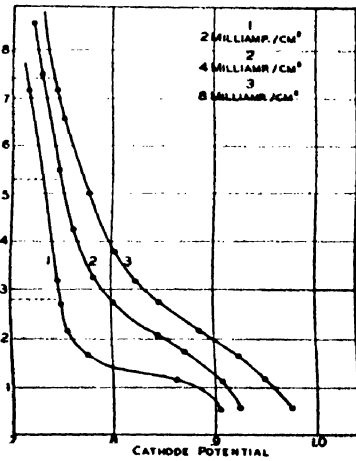


FIG. 2. The system nickel-thallium

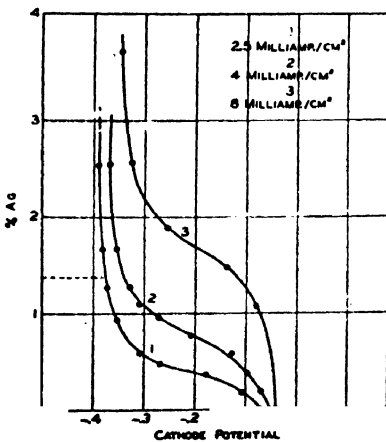


FIG. 3. The system copper-silver

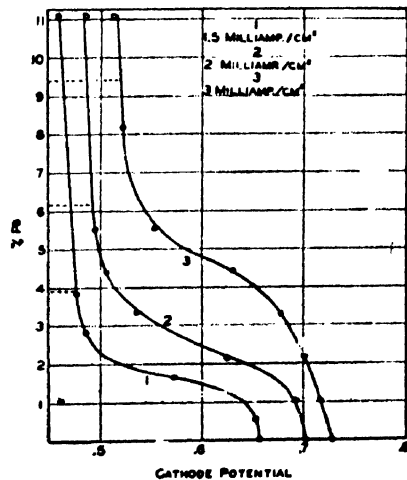


FIG. 4. The system lead-thallium

be determined by analysis or by the crystalline characteristics of the plate. All three methods were employed by the authors, depending upon which seemed best in a particular case. A difference of as large as 0.5 per cent in the value will have very little effect on the following discussion, excepting as to the values of empirical constants which might be varied a small amount. These limits of codeposition are indicated by the broken lines on the curves. As has been previously explained (4), it is nearly impossible to duplicate results involving nickel at high concentrations. This accounts for the absence of the lower portion of the curves in figure 2.

DISCUSSION

It has been pointed out by the authors that in plotting the limiting percentage composition of the solution against the logarithm of the current density, the curve will not be correct for the cases of large limit. However, if the ratio C_1/C_2 is employed, where C_1 is the concentration of the cation of lower cathode potential and C_2 the concentration of the higher, the discrepancy no longer exists. This function will give correct values in the limiting case, and also satisfy the experimental data. The letter l will be used to designate the limit expressed in this manner. In figure 5, l is plotted against the logarithm of the current density. The points fall on a straight line well within the experimental error.

If $\frac{lE_H}{E_L}$ is plotted against $\frac{1}{N}$ at constant current density the curves in figure 6 are obtained. E_H is the equivalent weight of the metal of higher cathode potential, E_L the equivalent weight of the metal of lower cathode potential, and N is the difference in cathode potential of the two ions involved. Curve I of figure 6 represents the values obtained for the case where the metals plating were both of the same valence. The values for l were calculated from previous data (2). Curve II shows the values obtained for the case where the cation of lower cathode potential is univalent and the cation of higher potential is bivalent. It will be noticed that nickel-thallium falls into this class. Nickel lies below thallium in the E.M.F. series. This shows in an excellent manner the shift of nickel in the series when current is passed through the reversible electrode making it irreversible (5). Curve III gives the values when the cation of lower cathode potential is bivalent and the one of higher potential is univalent. Inasmuch as all of these curves take into account the valence of the metals in the factor E_H/E_L , it is to be expected that they may be correlated by some simple function.

The curves are parabolic in form and give the following equations, where current density is expressed in milliamperes per square centimeter.

The constant in each case will be a function of the valence of the metals involved.

$$\text{I.} \quad l = 0.0524 \sqrt{\frac{1}{N}} \cdot \frac{E_L}{E_H} \log C.D.$$

$$\text{II.} \quad l = 0.00720 \sqrt{\frac{1}{N}} \cdot \frac{E_L}{E_H} \log C.D.$$

$$\text{III.} \quad l = 0.205 \sqrt{\frac{1}{N}} \cdot \frac{E_L}{E_H} \log C.D.$$

In the above equation $\frac{lE_H}{E_L}$ represents the ratio of charges carried by the cations at the limit of codeposition. If each charge was neutralized

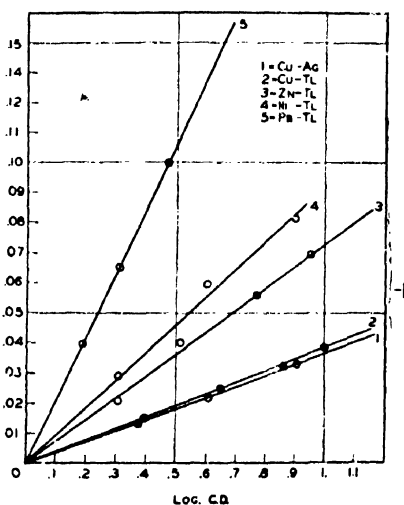


FIG. 5

FIG. 5. Plot of l against the logarithm of the current density

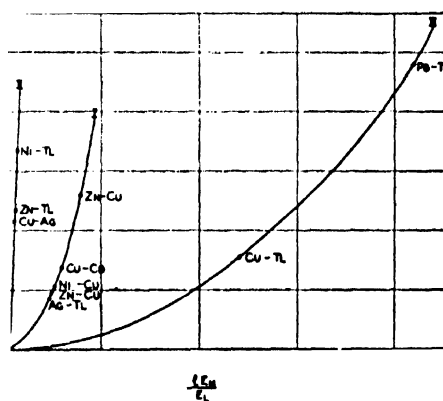


FIG. 6

FIG. 6. Plot of $\frac{lE_H}{E_L}$ against $\frac{1}{N}$ at constant current density

with equal facility, or if the ease of neutralization was only dependent upon the difference in cathode potential and the strength of the current density, then the ratio of the charges carried by the ions at the limit should be constant for any given difference in cathode potential at constant current density regardless of the valence of the metals involved.

In the case where the valence of the two cations is the same

$$l \frac{E_H}{E_L} = 0.0524 \sqrt{\frac{1}{N}} \log C.D. \quad (1)$$

If we double the valence of the cation of lower cathode potential we will have Case III. The ratio of the charges will be doubled, and therefore

the limit will be doubled if all the other variables are held constant. The ratio $\frac{E_H}{E_L}$ was doubled in the above operation, as E_L will be one-half its former value if its valence is doubled. With the stipulation that all variables excepting valence and limit be held constant, we must introduce a factor of 2 in order to take care of this change. We will then have,

$$l = 2 \times 0.0524 \sqrt{\frac{1}{N}} \times 2 \frac{E_L}{E_H} \log C.D. \quad (2)$$

or

$$l = 0.2046 \sqrt{\frac{1}{N}} \times \frac{E_L}{E_H} \log C.D. \quad (3)$$

This equation is in excellent agreement with the experimental data obtained.

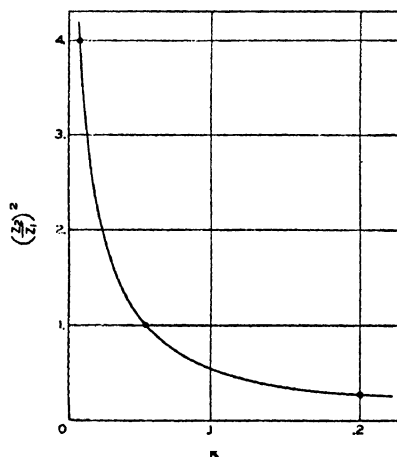


FIG. 7. Plot of $\left(\frac{Z_2}{Z_1}\right)^2$ against constant in equations I, II and III

For the second case, if we double the valence of the cation of higher cathode potential we will divide the ratio of the charges by 2. This will decrease the limit in the same proportion. Treating this case in the same manner as before, we have:

$$l = \frac{0.0524}{2} \sqrt{\frac{1}{N}} \times \frac{1}{2} \frac{E_L}{E_H} \log C.D. \quad (4)$$

or

$$l = 0.0132 \sqrt{\frac{1}{N}} \times \frac{E_L}{E_H} \log C.D. \quad (5)$$

This equation does not agree with the data, varying by a factor of approximately 2. It is most probable that the valence of the metal plating does have an effect not taken care of by the ratio of the equivalent

weights. It would seem that the tendency is for two univalent ions to plate more readily than a bivalent ion. This tendency would be augmented in the last case by the fact that it was also the ion of higher cathode potential, with less tendency to plate out. Just what this discrepancy is due to is being investigated.

CONCLUSION

In order to obtain an empirical expression for the variation of the constant in equations I, II, and III, $\left(\frac{Z_2}{Z_1}\right)^2$ was plotted against the constant. Z_1 is the valence of the ion of lower cathode potential, and Z_2 is the valence of the ion of higher potential. Figure 7 shows the curve obtained. It is hyperbolic in form and fits the equation,

$$l = \frac{0.066 Z_1^2 - 0.0087 Z_2^2}{Z_2^2 + 0.059 Z_1^2} \left(\sqrt{\frac{1}{N}} \times \frac{E_L}{E_H} \log C.D. \right) \quad (6)$$

where $C. D.$ is in milliamperes per square centimeter.

Substituting in equation 6 the following values for zinc-thallium and thallium-lead at 5 amperes per square foot,

	ZINC-THALLIUM	THALLIUM-LEAD
Z_1	1	2
Z_2	2	1
N	0.42	0.17
$\log C. D.$	0.74	0.74
E_L	204	102.5
E_H	32.7	204

we obtain

$$l_{Zn-Tl} = \frac{0.66 \times 1 - 0.0087 \times 4}{4 + 0.059} \times 4 \left(\sqrt{\frac{1}{0.42}} \times \frac{204}{327} \times 0.74 \right) \quad (7)$$

from which the per cent of thallium at the limit is 5.4. Calculated in the same manner the per cent of lead at the limit is 18. The values obtained for thallium-lead by Fink and Conrad (1) and for zinc-thallium by Parks and LeBaron (3) are 19 and 5.3, respectively. The agreement is excellent and serves as a good check on the validity of the method employed to calculate these limits.

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THE SOLUBILITY AND ACTIVITY COEFFICIENT OF SILVER IODATE IN POTASSIUM NITRATE SOLUTIONS. THE STANDARD POTENTIAL OF THE SILVER-SILVER IODATE ELECTRODE

I. M. KOLTHOFF AND J. J. LINGANE

School of Chemistry, University of Minnesota, Minneapolis, Minnesota

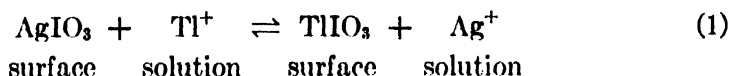
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In this study we have determined the solubility and activity coefficient of silver iodate in solutions of potassium nitrate up to an ionic strength of 1 molar, and have compared the experimental values with those calculated from the Debye-Hückel equation. We have also computed the standard potential of the silver-silver iodate electrode by combining the value obtained for the activity product of silver iodate with the standard potential of the silver electrode.

Silver iodate possesses distinct advantages, because the concentration both of the silver and of the iodate ions in the saturated solutions can be determined with an adequate degree of accuracy. In most studies of solubilities of slightly soluble salts the concentration of either the cation or the anion in the saturated solution is determined, and it is tacitly assumed that the equivalent concentration of the ion of opposite charge is equal to that of the ion which has been determined. When dealing with slightly soluble salts there are several reasons why an inequality of the concentrations of the cations and anions of the salt in the saturated solutions may be found. In the first place contamination of the slightly soluble salt by a salt having a common ion will cause such an inequality; in this case the difference between the concentration of the lattice cation and anion should increase with the amount of solid taken.

Furthermore, inequality may be caused by an exchange between lattice cations and cations in the surface of the glass container. Actually, it has been found in the present study that when the solubility of silver iodate is determined in uncoated glass containers, the concentration of the silver ions is smaller than that of the iodate. The error has been eliminated by coating the interior of the glass bottles with paraffin. Incidentally, it may be mentioned that Johnson (2) found an abnormally small value for the silver-ion concentration in a saturated solution of silver chloride in water, but in dilute nitric acid he obtained normal and reproducible values. The explanation of this abnormal behavior is that from neutral medium silver ions disappear by exchange with cations from the glass surface, whereas in acid medium hydrogen ions instead of silver ions give this exchange.

A third cause of inequality of the concentrations of lattice cation and anion in the saturated solutions in the presence of a foreign electrolyte is the possible exchange between foreign ions and lattice cations or lattice anions on the surface of the solid. A number of cases in which this type of exchange occurs have been studied in this laboratory (4). In the present study it was found that barium and thallium ions exchange with silver ions on the surface of silver iodate:



MATERIALS

Silver iodate: This salt was prepared by rapid precipitation, using thrice-recrystallized potassium iodate and pure silver nitrate. The precipitation was carried out at room temperature from dilute solutions, the potassium iodate solution being added to a slight excess of the silver nitrate solution. The product was aged for four days in the mother solution and was then washed with twelve separate portions of conductivity water, each portion being removed by centrifuging. It was then dried in a vacuum oven for ten hours at 55°C.

Part of the original product was recrystallized from a large volume of 1 *N* nitric acid. The product consisted of relatively large crystals which were thoroughly washed and were dried over fused potassium hydroxide.

Potassium nitrate: Commercial c.p. samples of the salt were recrystallized five times from conductivity water. The mother liquor from the third recrystallization was free of chloride. The salt was dried for several hours in an oven at 150°C.

Barium, lead, and thallous nitrates: These salts were purified by several recrystallizations, and careful tests showed that they were free of chloride.

Water: Conductivity water with an average specific conductance of 1.4×10^{-6} ohms⁻¹, was used for preparing all solutions.

Solutions were prepared by weighing out the appropriate amounts of the dried salts. Carefully calibrated weights and volumetric glassware were used. Concentrations are expressed in moles per liter of solution at 25°C.

EXPERIMENTAL TECHNIQUE

The solubility determinations were carried out by rotating samples of the silver iodate with the various solutions in a water thermostat at $25.00^\circ \pm 0.02^\circ\text{C}$. Brown glass bottles, coated inside with paraffin and closed with paraffined corks, were used.

The rate of solution of silver iodate was determined by placing 100 mg. of the unrecrystallized salt in 275 ml. of conductivity water in a con-

ductance cell at 25°C. and measuring the decrease in resistance with time while the solution was stirred with purified nitrogen. It was found that the resistance dropped to within 2 per cent of its final value after only 30 min. and solubility equilibrium was reached after 60 min., even with this small amount of solid and relatively inefficient gas stirring. In the actual solubility experiments the samples were rotated for at least three hours, which was therefore an ample time.

Samples of the saturated solutions for analysis were obtained without removing the bottles from the thermostat by using a filter pipet with a plug of absorbent cotton affixed to its tip. The first portion of solution withdrawn was used to rinse the cotton filter and pipet and was then discarded.

Methods of analysis

The saturated solutions were analyzed for both silver and iodate, using 100-ml. samples.

The concentration of silver was determined by potentiometric titration with 0.001 *N* potassium iodide solution, delivered from a carefully calibrated 10-ml. microburet. This method of titration has been described elsewhere (5). The titrations were accurate to ± 0.2 per cent.

The concentration of iodate was determined by iodometric titration with 0.01 *N* thiosulfate, using a calibrated microburet; the end point was readily detectable to ± 0.03 ml. Thiosulfate solutions were prepared fresh each day, and were carefully standardized against dilute standard potassium iodate solutions under the same conditions as in the titrations.

Special experiments showed that the small amount of silver present in the saturated silver iodate solutions, which precipitated as silver iodide during the titrations, was entirely without influence on the accuracy (± 0.3 per cent) of the iodate titrations.

INFLUENCE OF UNCOATED GLASS BOTTLES ON THE SOLUBILITY OF SILVER IODATE IN WATER

Two preliminary series of solubility determinations were carried out using plain uncoated glass bottles in one series and paraffined bottles in the other. The data obtained are given in table 1, in which the first column gives the amount of solid silver iodate used (original unrecrystallized product) and the third and fourth the silver- and iodate-ion concentrations in the saturated solutions. The observed solubility product L ($= C_{Ag^+} C_{IO_3^-}$) is given in the fifth column, and the square root of L is given in the last column.

These data show that the silver-ion concentration was about 15 per cent smaller than the iodate-ion concentration when plain glass bottles were used, whereas the concentrations were virtually equal in paraffined bottles.

It is interesting to note that the average solubility product using plain glass bottles was quite close to that using paraffined bottles, even though the individual ion concentrations were not equivalent.

TABLE 1

Influence of uncoated glass bottles on the solubility of silver iodate in water

Samples of the original unrecrystallized silver iodate rotated for at least three hours with 200 ml. of pure water at 25.00°C.

EXPT. NO.	AgIO ₃ IN GRAMS	NO. OF DETERMINATIONS	AVERAGE CONCENTRATION IN MOLES PER LITER $\times 10^4$		$L \times 10^3$	$\sqrt{L} \times 10^4$
			Silver	Iodate		
Plain uncoated bottles						
1.....	0.05	4	1.633	1.839	3.00	1.73
2.....	5.0	3	1.630	1.910	3.11	1.76
Paraffined bottles						
3.....	0.1	5	1.750	1.796	3.143	1.773
4.....	3.0	1	1.76	1.81	3.18	1.79
5.....	0.05	1	1.76	1.80	3.17	1.78
Average of paraffined bottles.....					3.152	1.776

TABLE 2

Exchange adsorption of barium and thallous ions with silver iodate

Unrecrystallized silver iodate rotated with the solutions in paraffined bottles for three hours at 25.00°C.

EXPT. NO.	SALT	AgIO ₃ IN GRAMS	CONCENTRATIONS IN MOLES PER LITER $\times 10^4$		$L \times 10^3$
			Silver	Iodate	
1.....	0.01 M Ba(NO ₃) ₂	0.05	2.11	2.14	4.52
		3.0	2.20	2.08	4.58
2.....	0.01 M TlNO ₃	0.05	2.00	1.98	3.96
		3.0	2.05	1.91	3.92

EXCHANGE ADSORPTION OF BARIUM AND THALLOUS IONS WITH SILVER IODATE

Experiments were carried out in which 0.05 g. and 3.0 g. of the original unrecrystallized silver iodate were rotated for three hours with 0.01 molar solutions of barium nitrate and thallous nitrate. At these concentrations the solubility products of barium and thallous iodates are not exceeded. The purpose of using the very small amount of solid was to obtain the solubility of the silver iodate in the salt solutions, since with a very small

amount of solid the exchange is negligibly small. The experiments with the large amount of silver iodate show the extent of the exchange reactions. The data are given in table 2, and show that the concentrations of the silver and iodate ions were practically equal when the small amount of solid was used, but with the large amount of solid (much greater surface) the silver-ion concentrations were greater than the iodate-ion concentrations.

It is evident therefore that both barium and thallous ions exchange with silver ions on the surface of silver iodate, according to equation 1.

SOLUBILITY AND ACTIVITY COEFFICIENT OF SILVER IODATE IN POTASSIUM NITRATE SOLUTIONS

The solubility of silver iodate in potassium nitrate solutions in the concentration range from zero to 1 molar was next investigated. The recrystallized silver iodate and the paraffined bottles were used in these experiments. The data obtained are given in table 3. The square root of the solubility product is given in the fourth column, and the total ionic strength, S , in the fifth.

The relation between the activity product, K , the solubility product, L , and the ionic strength of the solutions, S , is given by

$$\log L^{1/2} = \log K^{1/2} + \frac{0.5045 S^{1/2}}{1 + 0.328 a S^{1/2}} \quad (1)$$

in which the last term is the Debye-Hückel expression for the negative logarithm of the activity coefficient, and a is the ion size parameter.

The value of K was obtained in the usual way by plotting $\log L^{1/2}$ against $S^{1/2}$, and extrapolating to zero ionic strength. The value of K found in this way was 1.744×10^{-4} , from which the value of the activity product K is $(1.744 \times 10^{-4})^2 = 3.042 \times 10^{-8}$.

The observed values of the activity coefficient, $f_{\text{obs.}}$, given in the sixth column of table 3 were computed by the relation

$$f_{\text{obs.}} = \frac{K^{1/2}}{L^{1/2}} \quad (2)$$

The values of $f_{\text{D.H.L.E.}}$ given in the seventh column were computed by the Debye-Hückel limiting expression, which at 25°C. is

$$-\log f = 0.5045 S^{1/2} \quad (3)$$

It will be observed that the activity coefficient is given accurately by the simple limiting Debye-Hückel expression up to an ionic strength of about 0.01 molar. At higher ionic strengths up to 1 molar the activity coefficient is given by the relation

$$-\log f = \frac{0.5045 S^{1/2}}{1 + 0.394 S^{1/2}} \quad (4)$$

which has been obtained from the Debye-Hückel equation by introducing the average value of a (1.2 A. U.) given in table 3. The values of a given in the last column of table 3 were obtained from $f_{\text{obs.}}$ at each ionic strength by means of the Debye-Hückel relation.

Kohlrausch (3) determined the solubility of silver iodate at a series of temperatures between 10°C. and 27°C., by the conductance method. A short interpolation of his data gives a value of 1.79×10^{-4} molar at 25°C., which is in good agreement with the value 1.771×10^{-4} molar found in the present study. Noyes and Kohr³ found a value of 1.89×10^{-4} molar at 25°C. by a gravimetric method involving the precipitation and weighing of silver iodide. It is evident, in view of the good agreement

TABLE 3

Solubility and activity coefficient of silver iodate in potassium nitrate solutions

Approximately 0.3 g. of recrystallized silver iodate rotated with 200 ml. of solution in paraffined bottles for at least three hours at 25.00°C.

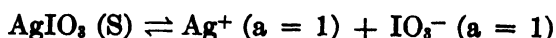
EXPT. NO.	KNO ₃ IN MOLES PER LITER	CONCENTRATIONS IN MOLES PER LITER × 10 ⁴		\sqrt{I} × 10 ⁴	S	$f_{\text{obs.}}$	$f_{\text{D.H.L.E.}}$	a IN A.U.
		Silver	Iodate					
1....				1.744*		(1.000)	(1.000)	
2....	0	1.761†	1.780†	1.771	0.000177	0.985	0.985	
3....	0.001301	1.813	1.832	1.823	0.001483	0.957	0.957	
4....	0.003252	1.863	1.877	1.870	0.003439	0.933	0.935	
5....	0.006503	1.908	1.919	1.914	0.006694	0.911	0.910	
6....	0.01410	1.991	1.996	1.994	0.01430	0.875	0.871	0.9
7....	0.07050	2.302	2.300	2.301	0.07073	0.758	0.736	1.3
8....	0.1998	2.668	2.663	2.665	0.2001	0.654	0.598	1.5
9....	0.4995	3.345	3.284	3.314	0.4998	0.526		1.2
10....	0.9989	4.087	4.086	4.086	0.9993	0.427		1.1
Average.....								1.2

* Extrapolated value.

† Average of three experiments.

between Kohlrausch's data and ours, that this value of Noyes and Kohr is too high, probably because of the analytical difficulties involved in their method.

From the value of K found in this study (3.04×10^{-8}) we find for the standard free energy change of the reaction



$\Delta F_{298}^0 = -2.303 RT \log K = 10,250 \text{ cal.}$ From Kohlrausch's data we find

$$\left(\frac{d \log K}{dT} \right)_{298} = 0.03496 \text{ deg.}^{-1}$$

Therefore

$$\Delta H_{298}^0 = 2.303 RT^2 \left(\frac{d \log K}{dT} \right) = 14,200 \text{ cal.}$$

or the heat evolved in the precipitation of 1 mole of silver iodate from an infinite volume of solution in which the activities of the silver and iodate ions are both unity is + 14,200 cal. at 25°C.

Greensfelder and Latimer (1) derived from Kohlrausch's data the following values: $\Delta F_{298}^0 = 10,233$ cal. per mole, and $\Delta H_{298}^0 = 14,478$ cal. per mole, with which our values are in fair agreement.

THE STANDARD POTENTIAL OF THE SILVER-SILVER IODATE ELECTRODE

The relation between the standard potential of the silver-silver iodate electrode, IO_3^- ($a = 1$), $\text{AgIO}_3(\text{S})/\text{Ag}$, the activity product of silver iodate, and the standard potential of the silver electrode is (7)

$$E_{\text{AgIO}_3}^0 = E_{\text{Ag}^+, \text{Ag}}^0 + \frac{RT}{F} \ln K \quad (5)$$

Combining the value of K found in this study with the value $E_{\text{Ag}^+, \text{Ag}}^0 = 0.7996$ v., computed by Lingane and Larson (7), we find for the standard potential of the silver-silver iodate electrode, IO_3^- ($a = 1$), $\text{AgIO}_3(\text{S})/\text{Ag}$

$$E_{\text{AgIO}_3}^0 = 0.7996 + 0.05913 \log (3.04 \times 10^{-8}) = 0.3551 \text{ v.} \quad (6)$$

This result is 1.8 mv. less than the value 0.3569 v. obtained by Pearce and Wirth (9) by direct measurements of cells of the type



which involve a liquid-junction potential. By keeping the concentration of the potassium chloride equal to that of the potassium iodate, Pearce and Wirth were able to correct for the liquid-junction potential by the Lewis and Sargent equation (6). They measured only three cells in the concentration range 0.01 to 0.10 M , in which the correction for the liquid-junction potential amounted to 7.5 to 8.7 mv. In obtaining their final value of $E_{\text{AgIO}_3}^0$ they discarded the results obtained with the most dilute electrolyte, so that the value 0.3569 v. is actually based on measurements of only two cells. It is interesting to note that the value obtained with the most dilute electrolyte which they discarded was 0.3553 v., which is in good agreement with the value that we have computed.

In view of the uncertainties involved in the measurements of Pearce and Wirth we believe that the value 0.3551 v. is the most reliable for $E_{\text{AgIO}_3}^0$.

We believe that the value of $K(3.04 \times 10^{-8})$ found in this study is correct

to at least ± 0.6 per cent. It follows therefore that the corresponding error in $E_{\text{AgIO}_3}^0$, due to this small uncertainty in K would be only

$$\Delta E_{\text{AgIO}_3}^0 = 0.0591 \log \frac{K_2}{K_1} = 0.0591 \log 1.006 = \pm 0.15 \text{ mv.} \quad (7)$$

which is of the same order of magnitude as the uncertainty in $E_{\text{Ag}^+, \text{Ag}}^0$.

It is evident therefore that the value $E_{\text{AgIO}_3}^0 = 0.3551 \text{ v.}$ is probably correct to at least $\pm 0.2 \text{ mv.}$

SUMMARY

1. In this study the solubility and activity coefficient of silver iodate in potassium nitrate solutions have been investigated up to an ionic strength of 1 molar. The concentrations of both silver and iodate ions in the saturated solutions were determined. The activity product of silver iodate at 25°C. was found to be 3.04×10^{-8} .

2. It was shown that saturated solutions of silver iodate in pure water contain a greater concentration of iodate than of silver ions, when uncoated glass vessels are used. This is attributed to an exchange between cations in the glass surface and silver ions in the solutions. The error resulting from this exchange was eliminated by coating the glass vessels with paraffin.

3. It was found that barium and thallous ions exchange with silver ions on the surface of silver iodate.

4. The standard potential of the silver-silver iodate electrode IO_3^- ($a = 1$), $\text{AgIO}_3(\text{S})/\text{Ag}$, was computed from the activity product of silver iodate and found to be $0.3551 \pm 0.0002 \text{ v.}$ at 25°C.

We express our appreciation to the Graduate School of the University of Minnesota for financial assistance in this work.

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ON THE MOVEMENT OF MATERIALS ACROSS LIVING MEMBRANES AGAINST CONCENTRATION GRADIENTS¹

RAYMOND C. INGRAHAM, HOWARD C. PETERS, AND
MAURICE B. VISSCHER

Department of Physiology, University of Minnesota, Minneapolis, Minnesota

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The ability of living systems to move materials against concentration gradients is one of their most important characteristics. Life under changing circumstances would be impossible without this ability. This generalization is as valid for complex organisms as it is for the simplest forms. The living organism must maintain its internal environment relatively constant in spite of changes in its external environment in order to maintain its integrity. In order to keep its salt content constant an organism must be able to do osmotic work. One of the most important cases is in connection with sodium chloride. In order to maintain constancy of composition with respect to this important component of the body, higher organisms must be able to prevent its loss from the intestines and kidneys when the rate of its intake is low and bring about its excretion when its intake is high. The problem of how salt may be moved against its diffusion gradients in accomplishing these ends is the subject of this paper.

The problem has been approached by a study of the circumstances surrounding the movement of salts against their concentration gradients from the intestine to the blood. It has long been known that all of the phenomena of intestinal absorption could not be accounted for on the assumption that the intestinal epithelium behaves like a dialyzing membrane. Reid (9) showed that fluid is moved across various epithelial tissues when there is no difference in osmotic pressure on the two sides. Heidenhain (4) found that water is absorbed from hypertonic solutions in the intestine. Goldschmidt and Dayton (2) found that in the case of solutions containing both sulfate and chloride, the latter was absorbed when its concentration was less than the concentration of chloride in the blood. Burns and Visscher (1) made an exhaustive study of the influence of various anions upon the movement of chloride into and out of the gut in the living animal. They found that in the presence of a sodium salt of

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sulfate, phosphate, citrate, or ferrocyanide, sodium chloride was very rapidly absorbed from the intestine against steep concentration gradients. Ingraham and Visscher (5, 6, 7, 8) have studied this problem further and have found, among other facts, that under favorable circumstances sodium chloride removal may proceed until the concentration ratio for chloride between blood and intestinal fluid may be 200 to 1. Details of methods will be found in these papers.

In figure 1 are the analytical results of a typical experiment showing sodium chloride removal. A solution isotonic with the blood plasma containing equi-osmotic fractions of sodium chloride and sodium sulfate was placed in a closed loop of lower small intestine. In one and one-half hours the concentration of chloride had fallen to 2.5 mg. per cent, or less than 1 per cent of the blood concentration. This occurred by movement into the blood. Obviously, osmotic work was performed by the system in moving chloride from a place of lower to one of higher concentration.

Also shown in figure 1 are the respective concentrations of ammonia in the intestinal fluid and in the blood. The ammonia is a product of the metabolism of the intestinal epithelium, and its relation to the activity of the intestine is seen in connection with the action of certain toxic substances which abolish the ability of the intestine to perform osmotic work; this will be referred to later.

The ability to do osmotic work is not specific for sodium chloride, for under suitable conditions it may be shown that sodium bromide moves at exactly the same rate against equally great concentration gradients (5). Moreover, this univalent ion impoverishment in the presence of polyvalent ions of the same sign is not limited to the anions, for when a polyvalent cation is present the univalent cation is likewise moved against large concentration gradients (8).

These phenomena are dependent upon certain specific properties of intestinal epithelium. This can be seen from results of the experiments in which specific poisons have been used (7). As little as 0.0001 *M* mercuric chloride stops the process of specific impoverishment, as does 0.0005 *M* Na_2HAsO_3 . Somewhat higher concentrations of sodium fluoride, hydrogen sulfide, and sodium cyanide produce a similar poisoning. In figure 2 the results are presented of a typical experiment on this question. Two adjacent loops of small intestine (lower ileum) of a dog were filled each with 100 cc. of an isotonic solution containing initially equi-osmotic quantities of sodium sulfate and sodium chloride. To the fluid in one loop there was added 0.025 *M* sodium fluoride. The results of the two experiments are plotted together, the one marked "control" and the other "NaF." In the case of the control the chloride content of the intestinal fluid fell to 22 mg. per cent in the course of 90 min., whereas in the loop containing sodium fluoride the chloride concentration instead rose to

approach the blood plasma level of 340 mg. per cent. The sodium fluoride destroyed the impermeability of the membrane to sulfate (not shown in the graph) and abolished the specific absorption. It also practically abolished the ammonia formation. These effects are produced by all of the poisons mentioned (7).

The conditions for the occurrence of specific absorption from the intestine are extremely exact. If the tissues are injured in any way, chemically, mechanically, or thermally, the epithelium is no longer able to perform osmotic work. The amount of work performed in a given time is not identical for different individual experiments, although from the same animal adjacent loops of intestine give almost identical results, and suc-

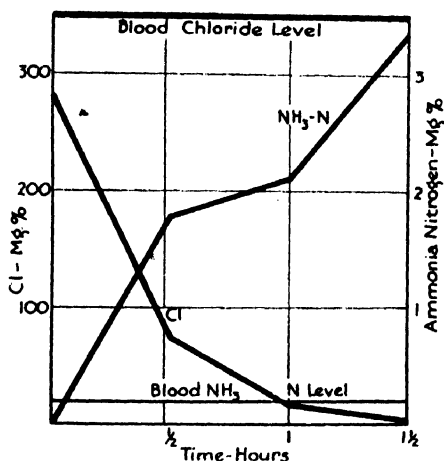


FIG. 1

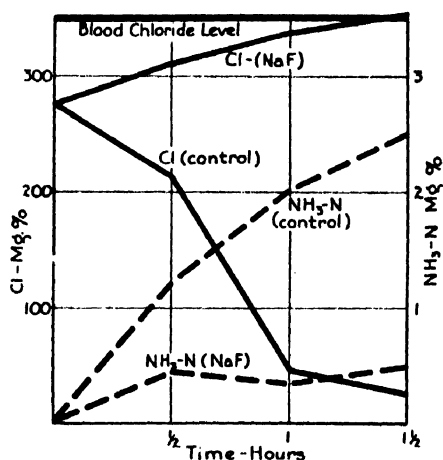


FIG. 2

FIG. 1. Results of a typical experiment showing sodium chloride removal. Also shown are respective concentrations of NH_3 in intestinal fluid and in the blood.

FIG. 2. Effect of sodium fluoride on intestinal membrane

cessive trials are in agreement. Occasionally the intestine of an animal shows spontaneously poor ability to do osmotic work. This might seem to be a disadvantage to the study of the phenomenon, and it is a disadvantage to the extent that a larger number of experiments have had to be performed than would have been necessary if the material were more uniform. However, one advantage has accrued from the instances of spontaneous failure of ability to do osmotic work, namely, that they have given opportunity for the study of means of bringing about more rapid performance of osmotic work. The most striking effect produced by any substance studied is that resulting from the addition of relatively small quantities of $\text{Al}(\text{OH})_3$. As a routine procedure in a number of experiments two adjacent loops of small intestine were studied, being filled with the

usual isotonic mixture of sodium chloride and sodium sulfate. In the case of one of the loops there was an addition of 1.5 cc. of alumina cream per 100 cc. of fluid. It was regularly found that the rate of chloride removal was greater from the loop containing the $\text{Al}(\text{OH})_3$ than from the control. This effect is shown in figure 3. In this instance there was very little Cl impoverishment in the control loop, whereas in that containing the alumina cream the chloride concentration fell to a low level. The same effect of aluminum was observed when small quantities of $\text{Al}_2(\text{SiO}_3)_3$ are employed. There is a suggestion that this effect depends upon the sign of the aluminum ion, since the negative colloidal dyes, trypan red and brilliant vital red, produce a reverse effect, whereas in a number of instances methylene blue has accelerated chloride impoverishment. The influence of methylene blue need not, of course, be due to the simple effect of charge, and the mechanism of the $\text{Al}(\text{OH})_3$ effect cannot be considered to be settled.

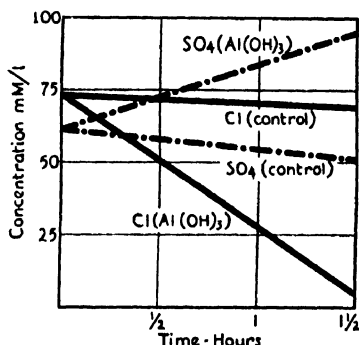


FIG. 3. Effect of $\text{Al}(\text{OH})_3$ on chloride removal

As has been pointed out in a previous publication (6) it has been found to be impossible to account for univalent ion impoverishment on the basis of a membrane equilibrium of the Donnan type, or as resulting from processes going on in approaching such equilibrium. After exhaustively considering and subsequently rejecting every known type of process based on ion exchange or membrane equilibrium, a kinetic picture has been developed, which is based upon highly probable assumptions and which, as will be apparent from the data presented, will satisfactorily account in a quantitative way for the phenomena as observed.

The type of uni-univalent salt impoverishment which is observed in the small intestine can be accounted for by assuming that there is a flow of water into the blood carrying out the uni-univalent salt at the concentration at which it exists in the gut, and a simultaneous flow of water free from that salt into the intestine at another point. It is necessary to postulate a membrane which is in essence a mosaic, one portion of which is strictly semipermeable and through which water enters the gut, and

another portion of which is permeable to uni-univalent salts through which the solution of such salts passes into the blood. This scheme is analogous to the physical model diagrammed in figure 4.

If the vessel contains originally V_0 liters of a solution of sodium chloride at a concentration C_0 millimoles per liter, and pure water flows into the vessel at some rate R_i and sodium chloride solution at a concentration C (the concentration at any time t) leaves the vessel at some rate R_o , the concentration, C , of sodium chloride in the vessel will decrease. If the rates of flow, R_o and R_i , are constant or vary in a uniform manner with time, the concentration, C , will likewise decrease in a uniform way with time. In the following derivation only the case in which R_i and R_o are constant is considered.

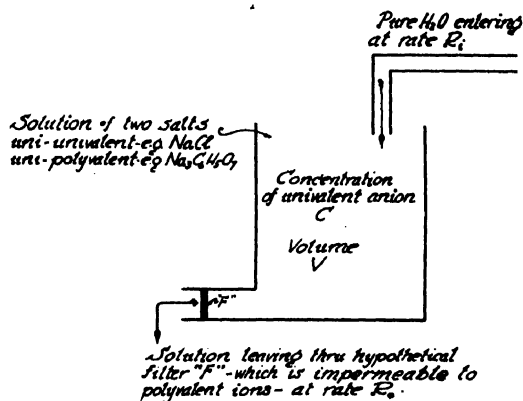


FIG. 4. Model for explaining the type of uni-univalent salt impoverishment which is observed in the small intestine.

In the case of the intestine the solution contains both sodium citrate and sodium chloride. The gut is freely permeable to sodium chloride but almost completely impermeable to sodium citrate. Then if a hypothetical filter, F , is assumed to be present at the outlet which is impermeable to sodium citrate, the above scheme will represent a physical model of the chloride-impoverishing mechanism of the small intestine on the basis of this theory.

If the rates R_o and R_i are constant it is possible to derive the mathematical relationship between concentration and time in terms of the original volume and concentration of the fluid in the intestine and the rates of fluid movement. By comparing the concentration of sodium chloride experimentally determined at various intervals of time in the course of an actual experiment with those values of C calculated from the theoretical formulae at the same time, one can determine whether chloride impoverish-

ment as it occurs in the small intestine can be quantitatively accounted for by the type of fluid movement postulated.

The formula relating time and concentration is derived as follows: Let

V_0 = the original volume of the solution in liters,

C_0 = the original concentration of sodium chloride in the solution in millimoles per liter,

V, C = the volume and concentration at any time t in the same units,
 t = time in hours,

R_0 = rate of flow of sodium chloride solution, concentration C , from the intestine to the blood in liters per hour,

R_i = the rate of flow of pure water into the intestine from the blood in liters per hour,

$D = (R_0 - R_i)$ or the rate of volume decrease, since in all experiments the volume in the intestine decreases with time, and

I = the amount of salt present at any time.

In such a system it is evident that:

$$C = f(I, V) \quad (1)$$

I and V are functions of the third variable t . The total derivative of equation 1 in respect to t is then:

$$\frac{dC}{dt} = \frac{\partial C}{\partial I} \frac{dI}{dt} + \frac{\partial C}{\partial V} \frac{dV}{dt} \quad (2)$$

At any time

$$C = \frac{I}{V} \quad (3)$$

Therefore,

$$\frac{\partial C}{\partial I} = \frac{1}{V} \quad (4)$$

$$\frac{\partial C}{\partial V} = -\frac{I}{V^2} \quad (5)$$

The change in salt content in respect to time $\left(\frac{dI}{dt}\right)$ is equal to the rate of exit of salt solution multiplied by the concentration of salt in the moving fluid, or,

$$\frac{dI}{dt} = -CR_0 \quad (6)$$

The change of volume with time is equal to the difference in the rate of fluid leaving and fluid entering:

$$\frac{dV}{dt} = (-R_0 + R_i) = -D \quad (7)$$

Substituting equations 4, 5, 6, and 7 for the proper terms in equation 2:

$$dC = \left[\frac{1}{V} (-CR_0) + \left(-\frac{I}{V^2} \right) (-D) \right] dt \quad (8)$$

From equations 3 and 7:

$$dC = \left[\frac{-CR_0}{V} - \frac{C}{V} (R_i - R_0) \right] dt \quad (9)$$

Simplifying:

$$dC = \left(\frac{-CR_i}{V} \right) dt \quad (10)$$

$$\frac{dC}{C} = \frac{-R_i dt}{V} \quad (11)$$

Since $V = V_0 - Dt$

(12)

$$\frac{dC}{C} = \frac{-R_i dt}{V_0 - Dt} \quad (13)$$

On integration this yields:

$$\log C = \frac{R_i}{D} \log (V_0 - Dt) + \log A \quad (14)$$

Or

$$C = A (V_0 - Dt)^{\frac{R_i}{D}} \quad (15)$$

At zero time

$$A = \frac{C_0}{V_0^{\frac{R_i}{D}}} \quad (16)$$

Therefore

$$\frac{C_0}{V_0^{\frac{R_i}{D}}} (V_0 - Dt)^{\frac{R_i}{D}} \quad (17)$$

Simplifying and from equation 12

$$C = C_0 \left(\frac{V}{V_0} \right)^{\frac{R_i}{D}} \quad (18)$$

Or, in logarithmic form,

$$\log_{10} \frac{C}{C_0} = \frac{R_i}{D} \log_{10} \frac{V}{V_0} \quad (19)$$

By plotting the $\log \frac{C}{C_0}$ against $\log \frac{V}{V_0}$ one should obtain a straight line,

the slope of which represents $\frac{R_i}{D}$, if the formulation fits the real phenomenon. The results of three of the most complete experiments we have performed are plotted in this way in figure 5. The experimental data and some of the calculations are given for these experiments in table 1. For the period of the first hour in each case there is substantially a straight-line relation between $\log \frac{C}{C_0}$ and $\log \frac{V}{V_0}$, as is predicted from this reasoning. For the point at one and one-half hours, there was in two instances a very considerable deviation from the predicted straight line. This does not appear to be a serious discrepancy, however, because the assumption that

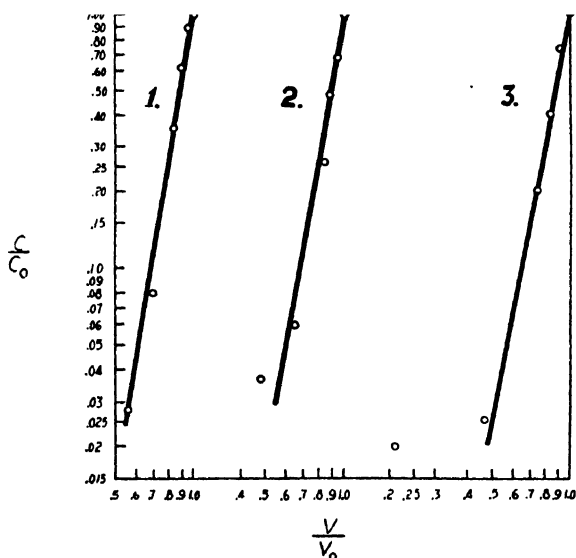


FIG. 5. Plot of $\log \frac{C}{C_0}$ against $\log \frac{V}{V_0}$

the membrane through which the water enters the gut is absolutely impermeable to chloride might be in error to the extent that perhaps 1 per cent of the chloride in the blood could pass. Such a minor correction as this could completely account for the deviation when the chloride content of the intestine has fallen to such low figures as 2 per cent of the blood chloride level. It should also be mentioned in this connection that one is here approaching the limits of analytical accuracy for chloride in biological fluids.

Summarizing the mathematical results, it seems that one is entitled to say that until extremely low chloride concentrations are reached the theory as developed will completely account for the phenomena observed.

From the values of $\frac{R_i}{D}$ the absolute value for R_i itself can be calculated because D is experimentally determined. In several experiments this value has ranged between 150 and 250 cc. per hour for a loop of intestine 25 cm. in length. It seems important to note that this is a distinctly reasonable result. R_i is in a mathematical sense an arbitrary constant as far as the data we have presented are concerned. It should be noted,

TABLE 1
Observed and calculated data on the rate of active absorption

TIME	C_{Cl} (EXPERIMENTAL)	$\frac{C}{C_0}$	V	$\frac{V}{V_0}$
Experiment 1				
hours	millimoles per liter		cc.	
0	77.9	1	50	1
0.167	69.2	0.89	47.5	0.95
0.333	48.2	0.62	44.4	0.89
0.583	28.1	0.36	41.4	0.83
1.00	6.24	0.08	35.3	0.70
1.50	2.2	0.028	28.0	0.56
Experiment 2				
0	59.5	1.00	75.0	1.00
0.167	40.1	0.67	70.7	0.94
0.333	28.7	0.48	66.3	0.88
0.5	15.6	0.26	62.0	0.83
1.00	3.5	0.059	49.0	0.65
1.5	2.2	0.037	36.0	0.48
Experiment 3				
0	59.7	1	75.0	1.00
0.17	43.5	0.73	68.3	0.91
0.33	23.8	0.40	62.0	0.82
0.50	12.05	0.20	55.3	0.74
1.00	1.56	0.026	35.7	0.47
1.50	1.2	0.020	16.0	0.21

however, that it is a factor amenable to measurement although not in a direct way, because fluid is both entering and leaving the intestine simultaneously. Up to the present time the best evidence that we have that water actually enters the intestine at the rate R_i is derived from the fact that values of this constant calculated from the movement of substances with widely different diffusion constants are in substantial agreement with one another.

The mechanism for driving water in this system has not been considered

up to this point. Since in these experiments there is no difference in osmotic pressure between the two fluids, ordinary osmosis will not account for the flow. Abnormal osmosis can, however, occur. Practical difficulties have prevented us from making crucial studies on this question up to the present time, and it would be unprofitable to go into an extended discussion from a theoretical basis, since too many important points are unknown. It is nevertheless worth while to say that the theory of Söllner (10) and of Grollman and Söllner (3) offers possibilities for the solution of this aspect of the problem.

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THE PERIODIC COAGULATION OF GOLD SOL IN THE PRESENCE OF COLLOIDAL SILICA

WILLIAM URE AND J. NORTON WILSON

Department of Chemistry, The University of British Columbia, Vancouver, Canada

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The Liesegang phenomenon of periodic precipitation in gels has not as yet received a general explanation, and the four principal theories advanced have been applied with partial success only to specific systems (1, 2, 7, 8). In the earlier treatment attention was focussed upon electrolyte concentration in relation to conditions of solubility and supersaturation. It was later shown, however, that in many cases ring systems could be readily formed by coagulation of substances originally dispersed as colloids in gels (5), and it appears likely that even when electrolytes interact the compound formed may exist primarily as a colloid, protected to some extent by the material of the gel.

The theory proposed by Dhar and Chatterji explains the ring formation as due to adsorption of colloidal particles by the coagulum which forms the ring (2). As a consequence a portion of the gel succeeding the ring is depleted more or less completely of colloidal material and the diffusing electrolyte must proceed further before coagulation again ensues. The chief function of the gel is then to peptize or protect the colloidal dispersion, as well of course as to provide structural support to the system. In support of these ideas it is shown that freshly formed precipitates may adsorb their peptized sols, and that there is a parallel between the protective action of gels and their power to cause rhythmic formations (3). Whether or not this explanation applies in all cases of ring formation it is evident that there must exist some sort of concentration limit with regard to the diffusing ions which may be a metastable supersaturation limit or a coagulation limit, but which determines the agglomeration of the precipitate. There are also cases where the colloid theory would seem to have no application,—in the periodic deposition of sodium chloride by salting out in capillaries, and in the reactions of gases diffusing in narrow tubes.

It is important that further information be collected as to the behavior of simple colloidal systems in which ring structures are produced on coagulation. The present work deals with a study of colloidal gold prepared in the presence of silica sol, the system setting to a gel either in the course

of time or through the influence of diffusing electrolytes. Stable red gold sols may be obtained in colloidal silica under carefully controlled conditions, the pH of the system being of prime importance. When setting was allowed to take place before introduction of electrolytes ring formation did not occur, the diffusing salts producing merely a change of color from red to blue. Apparently the protective action of the gel is sufficient to prevent extensive coagulation of the gold particles. It is possible, however, to adjust the pH of the gold-silica mixture to a point at which no gelation takes place on standing for a long period of time, and with these fluid mixtures the gold coagulated to form sharply defined rings when various electrolytes were allowed to diffuse in. Following the ring formation, setting to a gel took place under the influence of the advancing electrolyte and thus the structure was preserved. A study has been made of the conditions under which this interesting phenomenon takes place, and some conclusions have been drawn as to the bearing of these experiments on the theories of periodic structures.

EXPERIMENTAL

Materials

A commercial water-glass was diluted with three volumes of water and filtered through fuller's earth. A typical solution analyzed as follows: SiO_2 , 12.75 per cent; Na_2O , 6.11 per cent.

The nuclear gold sol was prepared by using 240 ml. of double-distilled water, 3.7 ml. of 0.25 per cent gold chloride solution, 4 ml. of 0.18 *N* potassium carbonate, and 0.8 ml. of a saturated solution of phosphorus in ether; this gave a deep red and very stable sol.

Dialysis was carried out in collodion sacs, while for diffusion membranes du Pont Cellophane No. 300 was cut into small squares and allowed to soak in water for at least two days before use.

Preparation of gold-silica sols

Experiments with various concentrations of water-glass and acid showed that with equal volumes of 1.16 sp. gr. water glass and 3 *N* hydrochloric acid a clear sol was obtained which would set to a gel in three or four days.

Before introduction of the gold this sol was dialyzed until no test for chloride was obtained. Dialysis was found to decrease the rate of setting both by removal of electrolyte and through actual loss of silica. In one experiment 34 per cent of the silica was thus removed. To reduce this loss sols were allowed to age for some eight hours before dialysis, which was then carried out for about twenty hours.

Colloidal gold was prepared by Zsigmondy's method of reduction of gold chloride by formaldehyde at 100°C. in the presence of potassium carbonate. Reduction was carried out directly in the silica sol, and in

most of the experiments 2 ml. of nuclear sol was added to produce uniform particle size. Following reduction the mixture was dialyzed for some forty-eight hours before the diffusion experiments were started.

It is important that the system be adjusted to a suitable pH before the gold is reduced. If the solution is too acid, reduction will be slow and incomplete, resulting in a blue or purple sol. On the other hand, the pH must not be too high if the silica is to set eventually. The influence of pH is shown in table 1, where 30-ml. samples of silica sol were adjusted to various pH values by addition of potassium carbonate and gold chloride, and the gold reduced by formaldehyde (without addition of nuclear sol). The results are somewhat variable but indicate that a pH in the neighborhood of 6.0 will produce a stable red gold sol which will set to a gel in a few days, whereas above this value stable silica sols may be maintained.

TABLE 1
Influence of pH upon set and stability of sols

pH	K ₂ CO ₃ (0.5 N)	AuCl ₃ (0.7 PER CENT)	SET	COLOR	STABILITY (AFTER 2 MONTHS)
	ml.	ml.			
4.70	0.3	2	Yes	Blue	
5.60	0.4	2	3 days	Red	Faded
5.90	0.45	2	5 days	Red	Blue-purple
5.90	0.6	2.5	4 days	Red	Good
5.95	0.60	2.5	4 days	Red	Murky
6.00	0.6	2	3 days	Red	Blue
6.00	0.7	2.5	5 days	Red	Purplish-red
6.05	0.55	2.5	4 days	Red	Good
6.20	0.75	2.5	9 days	Red	
6.30	0.8	2	No set	Red	
6.40	1.25	2	No set	Red	

pH values were obtained with the quinhydrone electrode, which is not entirely satisfactory in the presence of gold salts. It is possible to obtain the carbonate requirement by adding potassium carbonate to the silica sol before introduction of gold chloride and thus adjusting the pH, the buffer action of the carbonate being sufficient to prevent any large change. Some results from such procedure are shown in table 2 for a series of samples. All of these sols eventually set.

The preparation of a satisfactory sol which would not set on standing, but which could be set by electrolytes, was carried out as follows: A silica sol was made from 80 ml. of water-glass (1:3), 20 ml. of water, and 100 ml. of 3 N hydrochloric acid. After standing for nine hours it was dialyzed for twenty-four hours. To 150 ml. of this sol were then added 10 ml. of gold chloride solution (0.25 per cent) and 3 ml. of potassium carbonate solution

(0.5 *N*), bringing the pH to 6.2. Two ml. of nuclear sol was added, the mixture heated to 90°C., and 5 ml. of 0.2 per cent formaldehyde stirred in after removal of the flame. Reduction to clear red was complete in several minutes. Dialysis then took place for forty-eight hours. The resulting sol contained 1.79 per cent of SiO_2 .

Diffusion experiments

A series of test tubes was prepared containing gold-silica sol of pH about 6. Setting was allowed to take place, and the gels were overlaid with solutions of sodium chloride, sodium sulfate, potassium dihydrogen phosphate, magnesium chloride, and aluminum chloride at concentrations from 1 *M* to 0.025 *M*. In every case a continuous change from red to blue without ring formation was observed. A sol of pH 6.5 was now placed

TABLE 2
Carbonate requirement in reduction of gold

TITRATION OF SILICA 75 ML.		REDUCTION OF 5 ML. OF AuCl_3 WITH 1.5 ML. OF NUCLEAR SOL IN 75 ML. WITH 5 ML. OF FORMALDEHYDE		
Volume of K_2CO_3 ml.	pH	Extent of reduction	Time of reduction	Color
0.0	5.90			
0.4	6.50	Slight	Hours	Light blue
0.5	6.65	Slight	Hours	Purple
0.6	6.72	Complete	35 min.	Clear red
0.8	6.85	Complete	6 min.	Deep red
1.0	6.97	Complete	4 min.	Deep red

in a collodion sac immersed in a phosphate buffer solution of pH 6.24. As diffusion progressed the normal change from red to blue was accompanied by the formation of a series of dark rings, and setting of the sol took place.

For more convenient study of this process pieces of Pyrex tubing $\frac{3}{4}$ in. in diameter and 6 to 8 in. long were capped with Cellophane membranes secured by rubber bands, and filled with about 30 ml. of the gold-silica sol. The tubes were then set into Erlenmeyer flasks containing the diffusing electrolyte, and the whole placed in an air thermostat which was kept between 25° and 30°C. to 0.2°C. by means of two lamps and a mercury thermoregulator. A small fan was used to prevent local heating. Some of the structures obtained are illustrated in figure 1 for various electrolytes. The reproducibility is surprisingly poor even under these controlled conditions, as is shown in figure 1c for the same concentration of potassium chloride. Some difference in the permeability of the membranes is indicated. In some of the experiments three tubes with the sol were allowed

to dip into a large beaker containing the electrolyte solution, which was continuously stirred and covered with a layer of paraffin wax to prevent evaporation. Usually under these conditions the rings formed were observed to be regularly spaced, but even here puzzling discrepancies appeared. It appeared also that the light of the lamps was having an effect on the character of the rings but was not the prime cause, since similar periodic structures were also produced in the dark.

That there is some regularity in the spacing of the rings, at least in a considerable number of cases, is shown by the curves of figure 2, where the height of the ring as measured with a cathetometer is plotted against the ordinal number of the ring, starting with the lowest observable.

The effect of various electrolytes

With these sols, ring formation has been observed under the influence of sodium sulfate, sodium chloride, potassium chloride, silver nitrate, aluminum nitrate, aluminum chloride, and several buffer solutions at various concentrations. The behavior of the different electrolytes seems to be quite specific, and no direct effect of valence was noted, although some such effect is to be expected. Thus the same concentrations of potassium chloride and sodium chloride usually gave quite different results, and with the latter salt the results were much more uncertain than with the former, which could usually be relied upon to give regular systems. With barium chloride no definite rings were obtained, merely maxima and minima of density of coagulum. With 0.025 *N* aluminum chloride a system of very fine, closely spaced rings formed in the lower part of the tube and coarser rings in the upper part. Silver nitrate was found to produce effects like potassium chloride.

If the electrolyte is too concentrated the rings are indistinct. With decreasing concentration the ring system increases in sharpness to the point at which the silica will no longer set and the flocculated gold merely settles to the bottom of the tube. Comparison of ring systems was made using potassium chloride at a series of concentrations between 2 *N* and 0.015 *N*. Some of the results are shown in figure 3, and also in figure 1d. It is evident that decreasing the concentration of diffusing electrolyte decreases the number of rings, and increases the rate at which the distance between adjacent rings spreads out.

In some experiments the concentration of gold in the sol was varied by using amounts of gold chloride from 2.5 to 15 ml. per 150 ml. of sol. With increasing concentrations the rings increased in density, while at the highest concentration coagulation of the gold was incomplete, the spaces between the rings showing red gold colloid.

The setting of the silica was followed in a number of cases by means of a thin capillary tube of about 0.5 mm. outside diameter, which was carefully

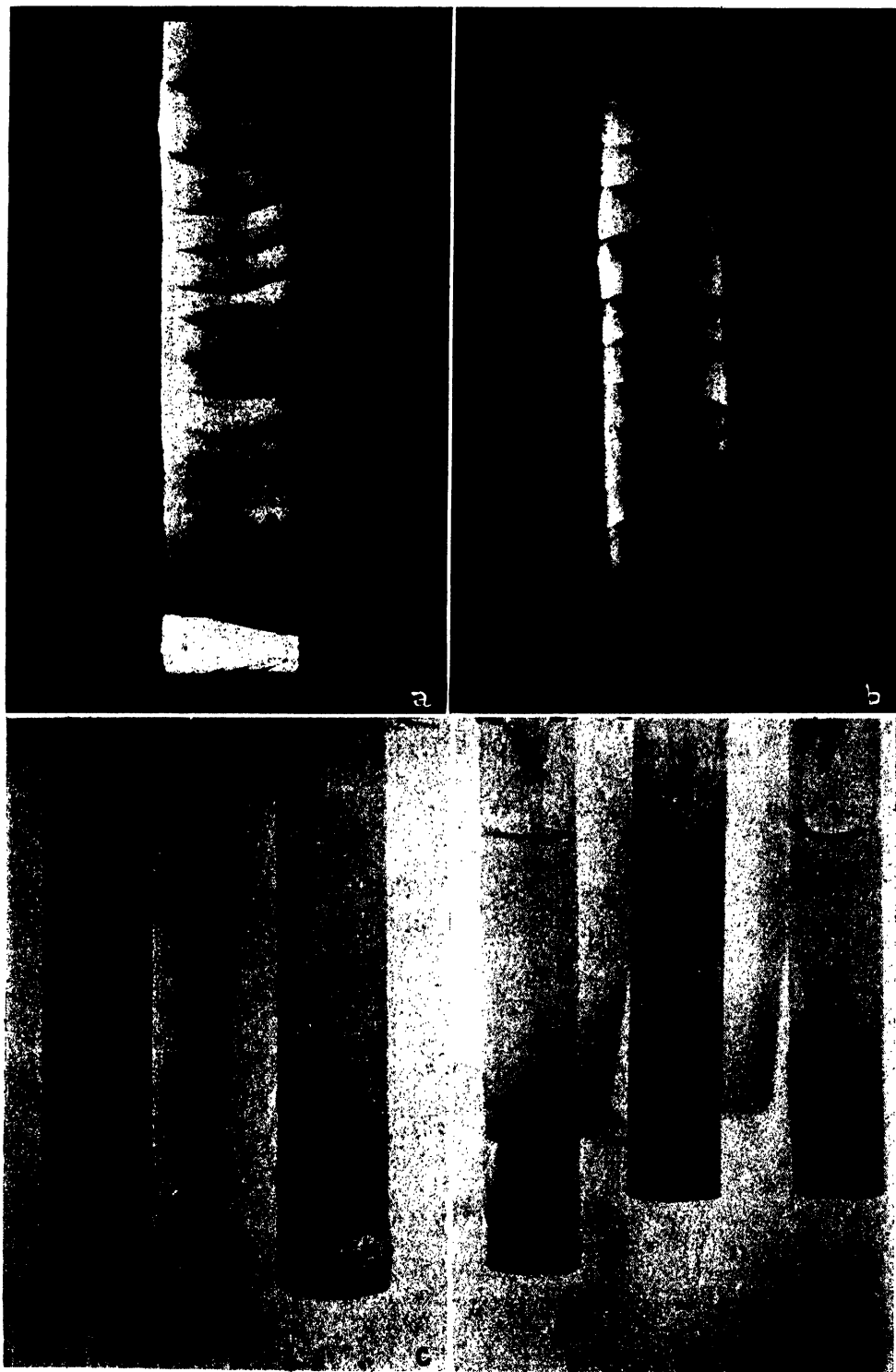


FIG. 1, a-d



FIG. 1 e, f

FIG. 1. Ring formation in gold-silica sols in the presence of various electrolytes. (a) With phosphate buffer; pH 7.7. (b) With 0.2 *M* aluminum nitrate; no membrane. (c) Regular and irregular rings produced with potassium chloride. (d) Effect of varying electrolyte concentration (0.015, 0.020, and 0.025 *N* potassium chloride). The gel prepared with 0.015 *N* potassium chloride is so weak that it will not stick in the tube. (e) Diffusion at various angles. (f) Potassium chloride, 0.015 *N*; sodium chloride, 0.025 *N*.

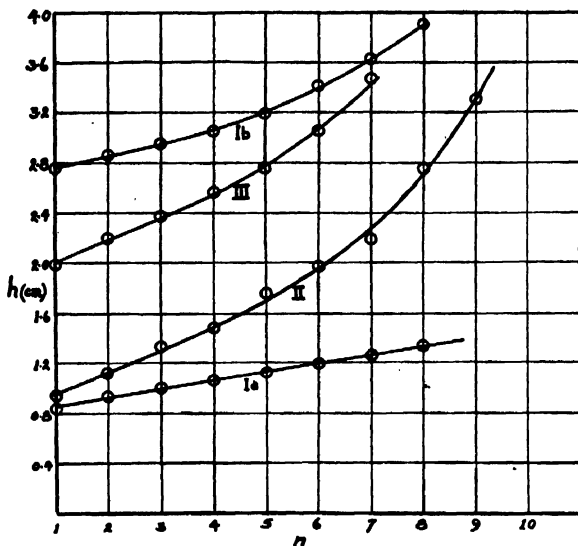


FIG. 2. Height of the ring plotted against the ordinal number of the ring. Curve I, 0.025 *N* aluminum chloride: (a) fine rings in lower part of tube; (b) coarser rings in upper part. Curve II, 0.025 *N* potassium chloride. Curve III, 0.025 *N* sodium chloride.

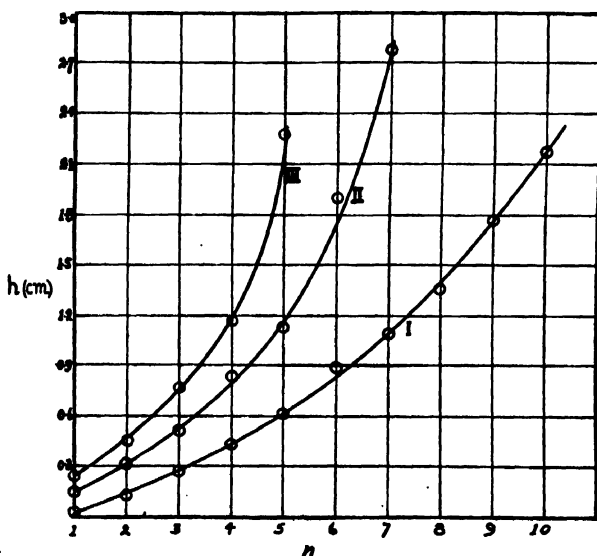


FIG. 3. Comparison of ring systems using potassium chloride in different concentrations. Curve I, 0.025 *N*; curve II, 0.020 *N*; curve III, 0.015 *N*.

thrust down the center of the tube as the rings were forming. The point at which the flexible tube began to bend as it was moved from side to side was taken as the approximate limit of the setting process. This was found

to be about 2 mm. behind the ring which was forming, but it is probable that the silica coagulates sufficiently to give support at the ring itself. The gel first formed is somewhat fluid, as shown by experiments in which the tubes were tilted from the vertical (figure 1e).

The function of the gel

It is apparent from the above that gel formation is necessary in these experiments for structural support. In a case where the electrolyte was allowed to diffuse from the top of the tube the gold was completely coagulated and fell to the bottom. With a horizontal tube a layer of coagulum was formed on the lower side of the tube.

There exists the possibility that the periodic phenomenon is confined to the silica in its setting, and that the coagulated gold merely serves to indicate the boundary between sol and gel. Such a gelation process has not as far as we know been observed, and would distinguish the systems here studied from those involving gels.

A series of tubes containing silica sol without gold were set up with 0.025 *N* potassium chloride diffusing upwards. After some hours fine black sand was dropped in from the top at the rate of a few grains every half-hour for about two days. No discontinuities were observed in the distribution of the particles. Similar results were obtained using emery powder and sulfur. When, however, the setting sol was overlaid with a suspension of silver chloride, a series of rings were formed as the silver chloride particles settled down. The success of the last experiment may be due to the smaller size of the particles used, but does not unequivocally indicate periodic gelation, since coagulation of the silver chloride particles under the influence of the upwardly diffusing electrolyte probably took place.

Further tests of this idea were based on the following considerations. The diffusion rate of electrolytes is slightly less in gels than in sols. Coagulation of the silica may be accompanied by adsorption of electrolyte. It is therefore possible that measurable discontinuities in the diffusion stream may occur. The diffusion of an electrolyte, silver nitrate, was therefore followed potentiometrically. Three diffusion tubes were set up containing in the first 0.001 *N* sodium nitrate, in the second silica sol without gold, and in the third a gold-silica sol. The tubes were dipped into a large beaker of 0.002 *N* silver nitrate, which was constantly stirred and protected from evaporation. Silver electrodes were let into the sides of the three tubes about 4 cm. above the membrane, and a single silver electrode was placed in the large beaker. Measurements of potentials between the reference electrode and the electrodes in the tubes were made simultaneously over a period of one hundred fifty hours during which the potentials dropped from about 175 to 20 mv. as the silver-ion concentration tended to equalize between the electrodes. Any changes in the rate of diffusion

in the tubes containing silica should be observable by comparison with the tube containing sodium nitrate solution. The curves obtained by plotting millivolts against time are not shown, since the values have no absolute significance. They were displaced from one another in the three cases, but were found to be almost parallel throughout. Certain irregularities in slope were found to be almost duplicated in the three cases, and must be attributed to changes in the membranes and in other external conditions. It is evident from this that no appreciable discontinuities of electrolyte diffusion are produced by the setting gel. During the course of the experiments a very regular ring system was formed in the tube containing the gold.

DISCUSSION

In common with other examples of the Liesegang phenomenon there appears to be in the systems studied here a general regularity with regard to the spacing of the rings. A number of expressions, mostly empirical, have been developed by various authors connecting the height, h , of the ring with its ordinal number, n . More fundamental treatment of periodic processes has been given by Morse and Pierce (6), and by Fricke (4). These authors, however, have confined their attention chiefly to the silver chromate rings in gelatin, and have treated the process from the point of view of opposing diffusion streams of electrolytes, with precipitation at supersaturation. In the present case we are dealing with the coagulation of a colloid by electrolytes, and it becomes necessary to consider a single diffusion stream and to replace the supersaturation limit of concentrations by some limit necessary to coagulation.

Using the same method of approach as that of Morse and Pierce, however, it is possible in our case to arrive at an equation for the distribution of the rings, which is based on the following assumption. There is necessary for coagulation of the gold particles a definite concentration of electrolyte, but, once started, coagulation can continue throughout the sol until some definite lower concentration of electrolyte is reached. This means, in effect, that the coagulum formed at the upper limit of concentration may remove particles by adsorption from a region between the higher and lower limits. It is also to be expected that the settling of the coagulated gold is rapid with respect to the advance of gelation, and that the latter corresponds to the advance of some definite concentration of electrolyte.

For the diffusion of the advancing electrolyte in the tube we have, according to Fick's equation,

$$a^2 \frac{\partial^2 u}{\partial x^2} = \frac{\partial u}{\partial t}$$

where a^2 is the diffusion coefficient, and u the concentration of electrolyte at the distance x from the starting point. It is assumed that the diffusion gradient is not affected by the formation of the coagulum, as the potentiometric measurements seem to show.

The solution of the equation is of the form

$$u = \frac{2U_0}{\sqrt{\pi}} \int_{\frac{x}{2a\sqrt{t}}}^{\infty} e^{-\beta^2} d\beta$$

where U_0 is the initial concentration of electrolyte and t is the time. Now if u is to be constant for the formation of each ring the lower limit of integration must be constant, and hence x/\sqrt{t} must be constant.

Let c_1 represent the electrolyte concentration at which the silica will set to a gel, c_2 the concentration at which the coagulation of the gold will take place, and c_3 the lower limit of concentration necessary to removal of the gold to the ring. From the experiments it is probable that c_1 and c_2 are not far different. Let h_1 , h_2 , and h_3 be the corresponding values of x at which these concentrations are reached at the time t . The gold in the region h_2 to h_3 has coagulated and accumulated at h_1 to form the ring.

Now for coagulation to set in again the concentration at h_3 must rise to the value c_2 . This will happen at a later time t' . Meanwhile the gelation has advanced to a point h'_1 . The gold from h_3 to some higher point h_4 will coagulate and fall to h'_1 , forming the next ring.

From the previous considerations we may set

$$h_2 = k_2 \sqrt{t} \quad \text{and} \quad h_3 = k_2 \sqrt{t'}$$

where k_2 is a constant, and at the time t

$$h_3 = k_3 \sqrt{t}$$

where k_3 is some other constant.

Hence

$$\sqrt{t'/t} = k_3/k_2$$

Also we have, at the rings themselves

$$h_1 = k_1 \sqrt{t} \quad \text{and} \quad h'_1 = k_1 \sqrt{t'}$$

Then

$$h'_1/h_1 = \sqrt{t'/t} = k_3/k_2 = \text{a constant}$$

In-general, for successive rings,

$$h_n/h_{n-1} = K$$

where n is the ordinal number of the ring. This equation has been proposed empirically by Schleussner (9). The final equation has been tested for these results by plotting the logarithm of h against n , since

$$h_n = Kh_{n-1} = K^{n-1}h_1$$

$$\log h_n = (n - 1) \log K + \log h_1$$

A straight line should be obtained. Some of the results obtained are shown in figure 4. While in a number of experiments little regularity was shown in the ring spacing, yet the more regular cases seemed to agree reasonably well with the equation given.

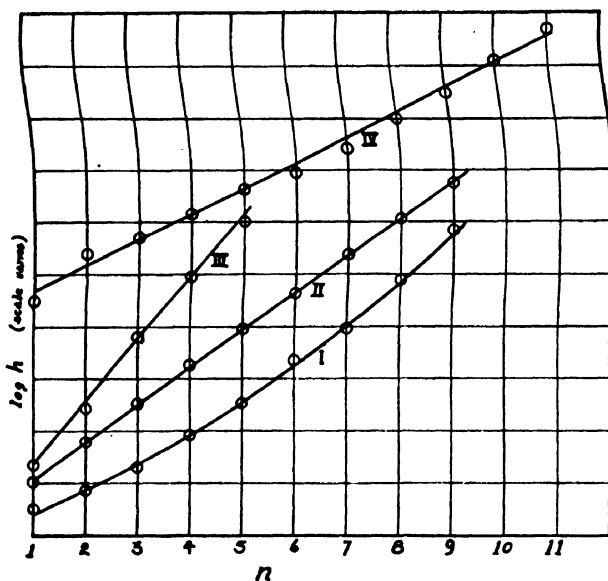


FIG. 4. Plot of $\log h$ against n . Curve I, 0.25 N potassium chloride; curve II, 0.025 N sodium chloride; curve III, 0.01 N potassium chloride; curve IV, 0.025 N potassium chloride.

In conclusion it should be noted that the mechanism outlined above is very probably not the only one which will lead to an equation for ring spacing of this type, and that similar results could be expected if the gel were setting in a discontinuous manner. The experiments described here may be interpreted to lend further support to the coagulation-adsorption theory as a reasonable explanation of a number of periodic processes.

SUMMARY

1. Experiments are described in which periodic coagulation is produced in colloidal gold in the presence of silica sol by diffusion of various electrolytes.

2. The effect of different electrolytes seems to be highly specific, but in general increase of concentration produces more closely spaced rings.

3. There appears to be no discontinuity in the diffusion of the electrolyte during ring formation and setting of the gel.

4. The results agree moderately well with the assumption that the coagulation of the colloid is accompanied by adsorption of colloidal particles in the adjacent region.

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THE SYSTEM SODIUM METASILICATE-WATER FROM 90°C. TO THE ICE POINT

CHESTER L. BAKER

Philadelphia Quartz Company, Philadelphia, Pennsylvania

AND

LING RALPH JUE

Philadelphia Quartz Company of California, Berkeley, California

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Sodium metasilicate seems to have been first reported by Fritzsche (2), who prepared the hydrates with six and nine molecules of water. Subsequent workers have reported more than a dozen different hydrates, the number of molecules of water ranging from two and a half to fourteen. The recent work of Baker, Woodward, and Pabst (1) indicates that probably only four hydrates exist. The characteristics of the hydrates with five, six, eight, and nine molecules of water as reported by them are given in table 1 for ready reference. Crystalline anhydrous sodium metasilicate has been prepared by Morey (5) from glasses and from hydrous systems at elevated temperatures. The characteristics of the anhydrous crystals as reported by Morey and Bowen (6) are also shown in table 1. The melting point for sodium metasilicate is that reported by Jaeger (4). The only published phase equilibrium studies involving hydrated sodium metasilicate are those of Harmon (3) for the system $\text{Na}_2\text{O}-\text{SiO}_2-\text{H}_2\text{O}$ at 25°C.

MATERIALS

The most satisfactory source of sodium metasilicate for the present work was found in specially prepared crystals of $\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$. The lower hydrates are less desirable because they are apt to carry inclusions and also to occlude small amounts of excess alkali. A solution carrying about 30 per cent Na_2SiO_3 was made up from a specially purified grade of commercial silicate of soda and c.p. sodium hydroxide. This solution was then allowed to stand for two weeks at room temperature. The crystals which separated were washed and centrifuged. After recrystallization they were usually found to be quite pure.

PROCEDURE

The solutions were made up by melting the $\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$ crystals in silver flasks and either adding the required amount of water or boiling off

any excess over that desired. The liquid was then adjusted to the thermostat temperature, and the flask was tightly closed and strapped onto a submerged rotor in the thermostat. Care was exercised to protect the metasilicate solutions from atmospheric carbon dioxide and never to bring them into contact with glass.

After a week or two of rotation in the thermostat, samples were taken of the aqueous phase and of the wet residue, and an analysis made of each. The particular flask was then replaced for another week or so, and then the contents again sampled and analyzed. This process was repeated until two or three successive analyses indicated that the system had come to equilibrium.

Once the approximate solubility was ascertained for a given temperature, two or more samples of undersaturated solution carrying in suspension an excess of crystals were usually started so as to approach equilibrium also from undersaturation. On the average, from six to ten

TABLE 1
Characteristics of sodium metasilicate and its hydrates

COMPOUND	CRYSTAL SYSTEM AND CLASS	DENSITY AT 20°C.	MEAN INDEX OF REFRACTION	MELTING POINT °C.
Na_2SiO_3	Orthorhombic		1.520	1088
$\text{Na}_2\text{SiO}_3 \cdot 5\text{H}_2\text{O}$	Triclinic pinacoidal	1.749	1.456	72.20
$\text{Na}_2\text{SiO}_3 \cdot 6\text{H}_2\text{O}$	Monoclinic sphenoidal	1.807	1.474	62.85
$\text{Na}_2\text{SiO}_3 \cdot 8\text{H}_2\text{O}$	Monoclinic prismatic	1.672	1.462	48.35
$\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$	Rhombic bipyramidal	1.646	1.455	47.85

weeks were required to establish the true solubility at any given temperature.

No particular difficulty was experienced at the lower temperatures, but as the solutions worked with became more concentrated, they were more viscous, slower to reach equilibrium, and more difficult to sample. In order to secure samples of the more viscous solutions, it was necessary to employ a special centrifuge operating at 5600 revolutions per minute. The strong tendency for these solutions to remain supersaturated is well illustrated by the ease with which it was possible to obtain a metastable point on the solubility curves for the pentahydrate and the octahydrate.

The hydrated crystals showed only a very small tendency to occlude excess Na_2O , although it can be said that the tendency became greater with lower degree of hydration. The anhydrous crystals, however, often occluded an appreciable excess of Na_2O . In one case, a solution originally carrying equimolecular proportions of sodium oxide and silica was found, after partial crystallization, to have only 0.95 mole of Na_2O per mole of

SiO_2 . The anhydrous crystals formed had a proportional excess of Na_2O . It was finally found necessary to prepare the required anhydrous metasilicate crystals, allow them to settle, drain off the mother liquor, add another saturated solution which was exactly congruent, allow the mixture to rotate in the thermostat for a week or so, and then again replace the mother liquor with a congruent one. This permitted the equilibrium solutions for each temperature study to be strictly congruent, although the crystals in equilibrium with them always contained a slight excess of Na_2O .

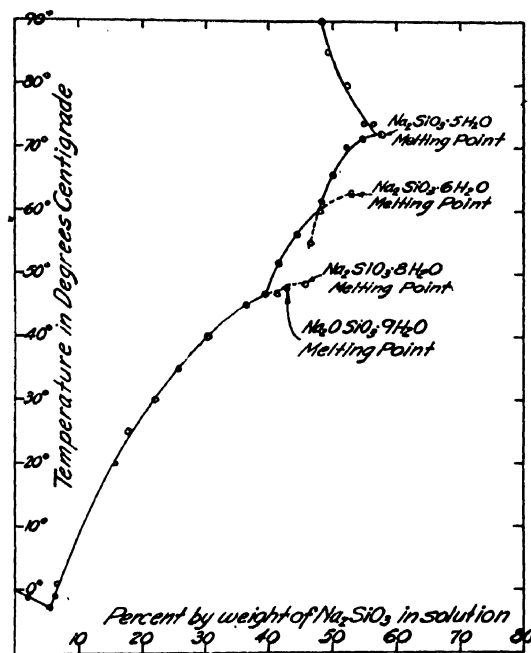


FIG. 1. The system sodium metasilicate-water from 90°C. to the ice point

The ice point was determined by rotating in a Dewar flask until analyses on successive days proved that equilibrium had been established. It is believed to be fairly accurate. The transition points were, in every case, determined by either extrapolation or interpolation, as indicated by the graphical representation (see figure 1). The melting points of the several hydrates are those earlier reported by Baker, Woodward, and Pabst (1).

SUMMARY

The phase equilibria for the system sodium metasilicate-water have been determined between 90°C. and the ice point. It is hoped that the phase equilibrium work on soluble silicate systems can be extended further and published in subsequent papers.

TABLE 2
Solubility data for the system sodium metasilicate-water

SOLID PHASE	TEMPERATURE	SOLUBILITY OF Na_2SiO_3
	°C.	per cent by weight
Ice.....	-1.00 ± 0.01	2.21 ± 0.1
Ice- $\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$	-2.7 ± 0.05	5.6 ± 0.1
$\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$	-1.00 ± 0.01	6.29 ± 0.1
	0.60 ± 0.01	6.63 ± 0.1
	20.00 ± 0.01	15.80 ± 0.1
	25.00 ± 0.01	18.20 ± 0.1
	29.90 ± 0.01	21.70 ± 0.1
	35.00 ± 0.01	25.66 ± 0.1
	39.90 ± 0.01	30.18 ± 0.1
	45.00 ± 0.01	36.18 ± 0.1
Melting point.....	47.85 ± 0.05	42.94
$\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$ $\text{Na}_2\text{SiO}_3 \cdot 8\text{H}_2\text{O}$ Metastable.....	47.6 ± 0.2	42.2 ± 0.5
$\text{Na}_2\text{SiO}_3 \cdot 8\text{H}_2\text{O}$	46.7 ± 0.01	41.3 ± 0.1
Melting point.....	48.35 ± 0.05	45.85
$\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$ $\text{Na}_2\text{SiO}_3 \cdot 6\text{H}_2\text{O}$	46.8 ± 0.1	39.80 ± 0.1
$\text{Na}_2\text{SiO}_3 \cdot 6\text{H}_2\text{O}$	47.00 ± 0.01	39.70 ± 0.1
	52.00 ± 0.01	42.00 ± 0.1
	56.00 ± 0.01	44.30 ± 0.1
	60.00 ± 0.01	48.31 ± 0.1
Melting point.....	62.85 ± 0.05	53.03
$\text{Na}_2\text{SiO}_3 \cdot 6\text{H}_2\text{O}$ $\text{Na}_2\text{SiO}_3 \cdot 5\text{H}_2\text{O}$	59.8 ± 0.1	48.0 ± 0.1
$\text{Na}_2\text{SiO}_3 \cdot 5\text{H}_2\text{O}$	55.00 ± 0.01	46.50 ± 0.1
	61.00 ± 0.01	48.25 ± 0.1
	65.00 ± 0.01	50.05 ± 0.1
	70.00 ± 0.01	52.40 ± 0.1
	71.30 ± 0.01	54.60 ± 0.1
Melting point.....	72.20 ± 0.05	57.53
$\text{Na}_2\text{SiO}_3 \cdot 5\text{H}_2\text{O}$ Na_2SiO_3	72.0 ± 0.1	56.6 ± 0.4
Na_2SiO_3	74.00 ± 0.01	55.75 ± 0.5
	74.00 ± 0.01	54.75 ± 0.5
	80.00 ± 0.01	61.63 ± 0.1
	85.00 ± 0.01	49.17 ± 0.1
	90.00 ± 0.01	47.97 ± 0.1

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STUDIES ON OVERVOLTAGE. IX
THE NATURE OF CATHODE AND ANODE DISCHARGE POTENTIALS AT SEVERAL
METAL SURFACES^{1,2}

A. L. FERGUSON AND S. KLEINHEKSEL

Department of Chemistry, University of Michigan, Ann Arbor, Michigan

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Polarization potentials have been measured, in general, by two methods commonly known as the direct and the commutator methods. Early investigators invariably found that the direct method gave higher values than the commutator method. For more than half a century the correct explanation has been sought for this discrepancy. The explanations offered fall largely into two groups. According to one group, the difference between the values given by the two methods is due to the existence of a resistance of some nature at the interface between electrode and electrolyte. This resistance has been named by different authors "surface resistance," "transfer resistance," "contact resistance," "film resistance," etc. According to the other group, the interrupting device used in connection with the commutator does not permit the total discharge potential to be measured because of the very rapid drop in potential during the interval between interruption of the current and measurement of the potential. Several years ago a thorough investigation of this subject was started in this laboratory. A brief summary of the work follows.

In the first paper (6) it was proven that the commutator gives values which are only averages. This provided a possible explanation for the observed discrepancies between the two methods since the commutator, therefore, could never give, directly, values as high as those obtained by the direct method.

In the second paper (7) a commutator of special design was used in an attempt to show that the potential at the beginning of the discharge interval is the same as that at the end of the charge interval. This was

¹ This paper is a portion of the dissertation submitted by Stanley Kleinheksel to the Faculty of the Graduate School of the University of Michigan in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

² The oscillograph used in these investigations was purchased with a grant from the Faculty Research Fund of the University of Michigan, which thus made this work possible.

not entirely successful, since it was not possible to measure the discharge potential at the instant the polarizing circuit was opened, and since the potential was dropping very rapidly at this time.

In the third paper (1) a new commutator was used that permitted charge potentials and corresponding discharge potentials to be measured within 0.0003 sec. from the time of interruption of the polarizing circuit. There was still, however, a discrepancy of a few millivolts between the measured potentials at the end of charge and the beginning of discharge. Certain other difficulties were also discovered that are inherent in the regular commutator potentiometer method and render it undesirable for the measurement of overvoltage and transfer resistance.

In the fourth paper (2) a commutator was used that permitted potentials to be measured practically simultaneously at several points during both the charge and discharge intervals. These results gave curves which could be extrapolated apparently with a high degree of accuracy to the instant of interruption of the polarizing circuit. The curves indicated that for platinized platinum in 2 *N* sulfuric acid at current densities between 3.8 and 150 ma. there is no surface resistance, but for smooth platinum the decrease in potential was so rapid as to make extrapolation highly uncertain.

The fifth paper (3) contains the description of a new device for the study of polarization potentials, known as a commutator oscillograph system. Actual photographs of the charge and discharge potentials throughout the complete cycle were obtained. This proved to be an excellent means for making a direct comparison of the commutator and direct methods. Oscillograms were taken by both the direct and commutator methods on the same film and practically at the same time and thus under identical conditions. These curves showed that the commutator gives a maximum value for charge potential that is identical with the value given by the direct method and confirmed the statement made in the second paper (7) that "the commutator and the direct methods would give the same values if measurements by the commutator method could be made at the instant the polarizing current is interrupted." The curves show, however, that for current densities of the order of 0.02 amp. it requires about 0.008 sec. for the cathode and 0.04 sec. for the anode to reach a maximum value. This means that, if the commutator is rotated at a speed too high to allow these time intervals for charge, correct values for charge will not be obtained. Investigators up to this time have generally used such high speeds in order to prevent the very rapid loss in potential at the beginning of discharge.

Those who support the idea that a resistance of some kind exists at the contact surface between electrode and electrolyte base their conclusions

upon the presence of an instantaneous drop in electrode potential immediately after the polarizing circuit is opened. This point of view is probably best represented by the work of Newbery (8) in which he used a cathode-ray oscillograph. He states, "The existence of this gap (a vertical displacement between charge and discharge curves) proves conclusively that there is an instantaneous fall of potential at the electrode the moment the exciting current is interrupted. . . . This resistance—transfer resistance—may be measured by observing the vertical height of the gap in the curves." In the seventh paper (4) an electromagnetic interrupter was substituted in place of the commutator. With this it was possible to determine the true nature of the decay curves by superimposing them directly upon another curve known to be due to an I.R. drop only, or on one known to be due to both an I.R. drop and the decay of a true electrode potential. It was evident, clearly, from the comparisons made of this nature, that there is no surface resistance at *platinized platinum* electrodes in 2 *N* sulfuric acid for current densities up to 0.017 amp.

In the eighth paper (5) the same method was used to study the nature of polarization phenomena at *smooth platinum* electrodes. It was found, however, that the early part of the potential decay curve dropped so rapidly that it could not be distinguished from a drop due to a pure resistance. It could not be demonstrated, therefore, that for such electrodes there is no surface resistance.

In the present investigation new equipment has been used with which it is possible to distinguish definitely between an I.R. drop and an electrode potential decay even for smooth platinum and several other materials investigated. With this equipment the decay of a true electrode potential may be distinguished from an I.R. drop in any case where the former requires more than 1×10^{-5} sec. per millivolt change in potential.

Overvoltage decay curves at the cathode were obtained for platinized platinum, smooth platinum, palladium, gold, silver, zinc, cadmium, antimony, and nickel. Decay curves at the anode were made for the first four. In each case curves were obtained at several current densities.

The method employed is fundamentally the same as that described in the last two papers (4, 5). In the present work, in order to be able to distinguish definitely in all cases between an I.R. drop and a true electrode potential decay, a new oscillograph vibrator (galvanometer) was used having a greatly increased frequency. In order to retain the desired sensitivity it was then necessary to construct a new amplifier having a much greater amplification; in fact, the sensitivity of the present system is actually 2.5 times that used previously.

The procedure is, essentially, to charge the cell under investigation for any desired period, then to interrupt the charging circuit at a definite

instant by means of an electromagnet, and finally to record the decay of potential photographically with the oscillograph. No current is drawn from the electrode under investigation.

The cell assembly is represented in figure 1 and needs no explanation except to state that the electrodes have an area of 1 sq. cm. and the backs are covered with paraffin.

It was found desirable to be able to obtain several sensitivities from the one amplifier. This was accomplished through a variation in the potential on the suppressor grid, G2, of the R.C.A. 57 tube (figure 2). Each different voltage value applied to the grid G2 required, however, a corresponding definite potential for grid G4 of the 2A3 tube. Six different combinations of voltages were used for grids G2 and G4, giving as many amplifier sensitivities designated as systems I, II, III, etc.; the first system produced the largest and the sixth the smallest sensitivity.

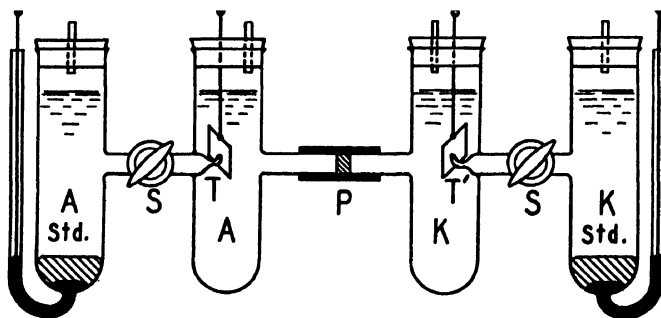


FIG. 1. Cell assembly

Each of the six systems required a separate calibration curve. A known potential E_g from a potentiometer applied to the control grid G1 of the amplifier, i.e., to the input leads (figure 2), produced a definite current I_p indicated by a milliammeter in the output circuit. A linear relation was found in the E_g - I_p curve between 60 and 130 ma. In order to locate the upper limit of the linear portion of the curve, it was only necessary, therefore, that the sum of all the potential differences in the input circuit should have a value such that the corresponding plate current was 130 ma. The oscillograph used required only 65 ma. for full scale deflection, which is well within the linear relationship. The upper limit of the linear portion for each amplification curve, in terms of milliamperes output, and the approximate sensitivity in terms of millivolts per milliamperes is given in table 1 for the six systems. The table contains, also, the corresponding E_{g2} and E_{g4} potentials.

A simplified diagram of the complete apparatus is given in figure 3. A potential divider, V, supplies the current for charging the electrodes. This circuit contains the cell under investigation and a standard 10-ohm

resistance, and is closed through contacts B3 - - B4 of electromagnet B. The value of the charging current is obtained from the measured potential drop across the standard resistance. Switch E represents a group of switches so arranged that the potential difference between any pair of the four electrodes,—anode standard, anode, cathode, or cathode standard,—

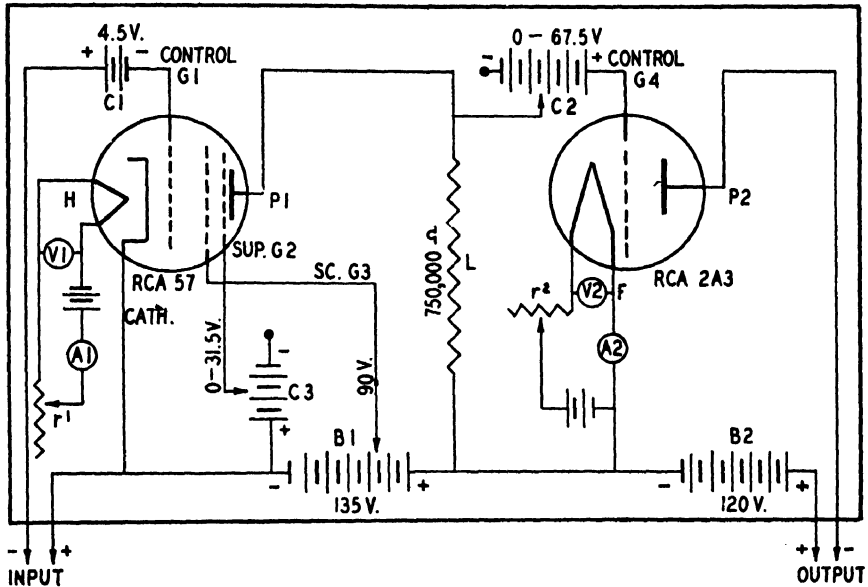


FIG. 2. D. C. amplifier

TABLE 1
Constants for the six amplification systems

SYSTEM NO.	Eg2	Eg4	OUTPUT CURRENT	APPROXIMATE SENSITIVITY
	volts	volts	ma.	mv. per ma.
I.....	0.0	67.5	130	1.0
II.....	-16.5	22.5	125	2.3
III.....	-25.5	10.5	120	4.5
IV.....	-28.5	6.0	120	7.3
V.....	-30.0	3.0	105	9.4
VI.....	-31.5	0.0	100	12.7

may be applied to either the potentiometer or the input of the amplifier. By means of the potential divider, V1, a potential may be placed in series with that of the cell under investigation. Since the potential to be measured is fixed, it is necessary to have this auxiliary potential from V1 in order to bring the current in the output circuit to the value corresponding to the upper limit of the linear portion of the characteristic curve of the

amplifier for the particular amplification system being used, i.e., 130 ma. for system I.

The output of the amplifier may be connected through switch A to either millimeter Am or to the sensitive element of the oscillograph. Since the linear portion of the characteristic curve of the amplifier, for system I for instance, lies between 130 ma. and 60 ma., but the oscillograph requires only 65 ma. for full scale deflection, the output of the amplifier is first connected to the millimeter and V1 adjusted to give 130 ma., and then an opposing potential from the divider V2 in the output circuit is inserted to reduce the current to the desired value, i.e., 65 ma. If the polarizing circuit of the cell is then opened, any potential drop in connection with

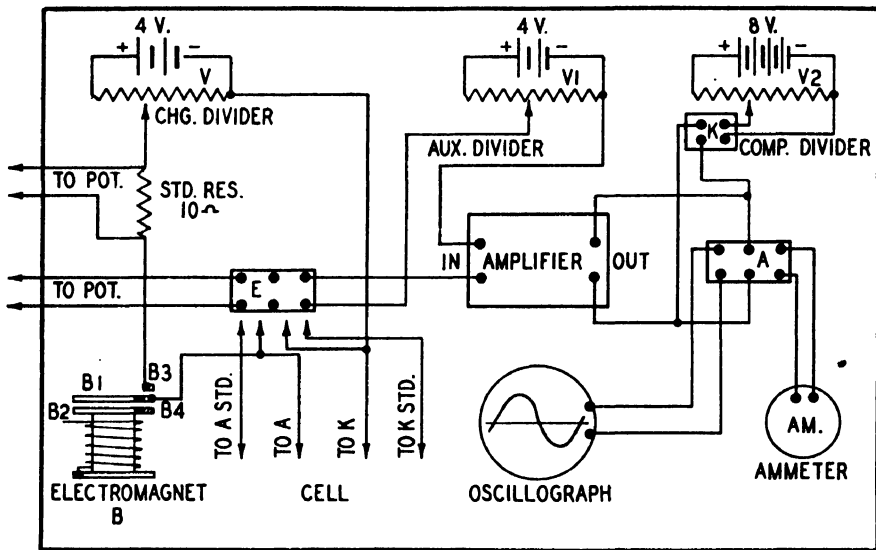


FIG. 3. Simplified diagram of apparatus

this cell and included in the input potential of the amplifier results in a decrease in plate current along the linear portion of the characteristic curve starting from 130 ma., but appears on the ammeter as a corresponding decrease from 65 ma. After such preliminary adjustments the ammeter is replaced by the oscillograph, which produces a permanent record upon the rotating film.

The resistances of the millimeter and the oscillograph element are nearly equal, so that no change in total resistance of the circuit is made when one is replaced by the other. Since the element of the oscillograph is in series with a portion of the potential divider V2, however, the resistance of the latter must be large compared to the former in order that the current change in the output circuit of the amplifier may be truly represented by the deflection of the oscillograph element. At no time was the

resistance included in the potential divider less than 200 times the resistance of the element. Experiments were carried out using various compensating potentials to shift the recorded curve to different positions from top to bottom of a calibrated film, and the potential indicated was entirely independent of the compensating potential, showing that the oscillograph records the true potential of the cell irrespective of the value of V2 used and therefore the position of the curve on the film.

In order to convert deflections of the light beam of the oscillograph which are recorded on the photographic film into volts, it is necessary to calibrate such recorded deflections in terms of applied potentials. To do this, first 60 mv. were applied from a potentiometer in the place of the cell. The potentials from V1 and V2 were then adjusted as described above to give 65 ma. through the oscillograph, which produced a line near the top of the film. With V1 and V2 left constant, the potential from the potentiometer was reduced 15 mv. and another line produced on the film which appeared slightly below the first. This operation was repeated until the whole film was calibrated. Separate calibrated films were made for each

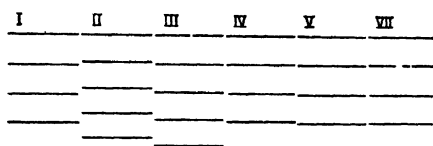


FIG. 4. Samples of calibrated films for the six amplification systems used

of the six amplification systems used. Samples of such films are shown in figure 4. New calibrations had to be made occasionally, owing to changes in the characteristics of the amplifier.

In all experiments the electrodes had an approximate exposed area of 1 sq. cm. and the back of the electrode was covered with paraffin. The electrolyte was 2 *N* sulfuric acid, which has a hydrogen-ion activity of nearly 1. Electrolysis was allowed to proceed for about one hour before measurements were taken. By this time the potentials had reached a constant value, the anode chamber had become saturated with oxygen and the cathode with hydrogen, and all other gases had been swept out.

Five different potentials were measured for each system used: anode vs. anode standard (A), anode vs. cathode standard (Ai), anode standard vs. cathode standard (I), cathode vs. cathode standard (K), and cathode vs. anode standard (Ki). The first gives the actual potential of the anode, the second gives this potential plus the I.R. drop through the solution, the third the I.R. drop through the solution alone, the fourth the actual cathode potential, and the fifth the cathode potential plus the I. R. drop through the solution.

The first electrodes worked with were platinized platinum. The

various decay curves are shown in figures 5 and 6. The only difference between the systems represented in the two figures is in current density. Several other current densities were used, but these are typical of all.

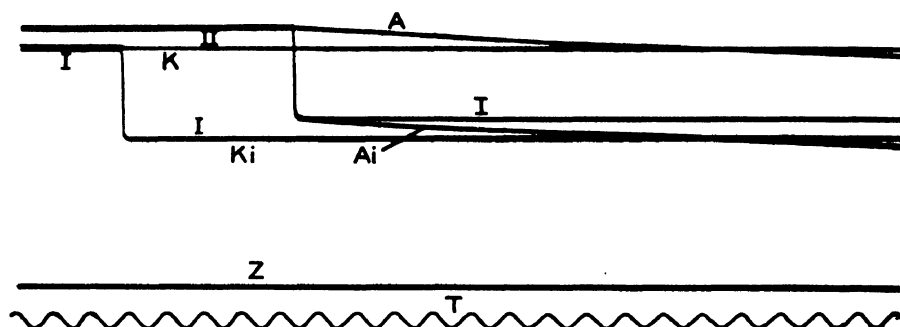


FIG. 5. Overvoltage decay curves for platinized platinum electrodes.
Amplifier system I

Curve	Potential measured	Value in volts	C. D. in milliamperes
A	Anode vs. anode standard	1.616	0.485
Ai	Anode vs. cathode standard	1.637	0.485
K	Cathode vs. cathode standard	0.008	0.485
Ki	Cathode vs. anode standard	0.029	0.485
I	Anode standard vs. cathode standard	0.021	
Z	Zero line of vibrator		

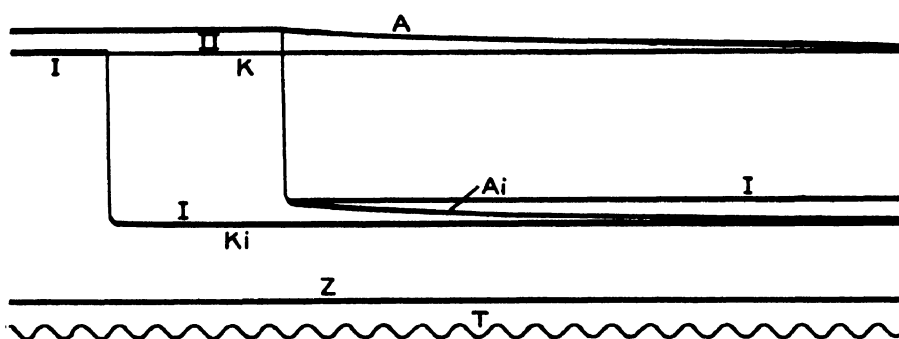


FIG. 6. Overvoltage decay curves for platinized platinum electrodes.
Amplifier system VI

Curve	Potential measured	Value in volts	C. D. in milliamperes
A	Anode vs. anode standard	1.840	9.05
Ai	Anode vs. cathode standard	2.336	9.05
K	Cathode vs. cathode standard	0.043	9.05
Ki	Cathode vs. anode standard	0.540	9.05
I	Anode standard vs. cathode standard	0.497	9.05
Z	Zero line of vibrator		

On each film there are two groups of curves, I and II, each made up of three curves. For instance, group II of figure 5 contains the curves A, Ai, and I. These are all superimposed at the start by the proper adjustment of V2. The point of separation of the curves represents the instant at which the polarizing current for the cell under investigation is interrupted. By means of various contact points on the rotating film drum this can be located at any desired time during the rotation of the film. One exposure is made to record the potential represented by A, another for Ai, and another for I. Group I is a similar set for the cathode. The base line for the undeflected vibrator element is represented by Z. The curve T represents a 120-cycle circuit. The films represented in these

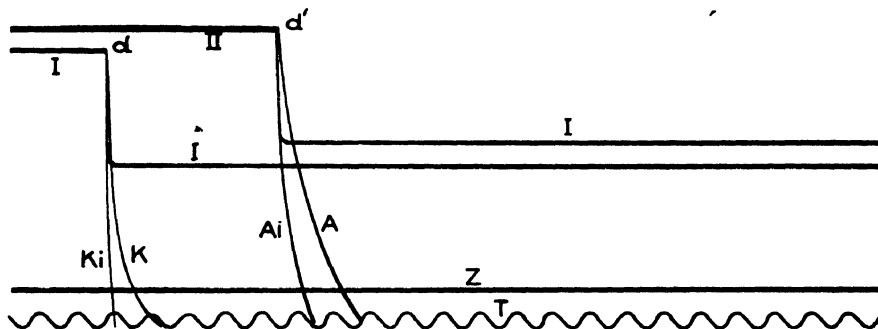


FIG. 7. Overvoltage decay curves for smooth platinum electrodes.
Amplifier system I

Curve	Potential measured	Value in volts	C. D. in milliamperes
A	Anode vs. anode standard	1.970	0.30
Ai	Anode vs. cathode standard	1.996	0.30
K	Cathode vs. cathode standard	0.107	0.30
Ki	Cathode vs. anode standard	0.133	0.30
I	Anode standard vs. cathode standard	0.026	
Z	Zero line of vibrator		

figures were, therefore, exposed eight times. In general the film speed was adjusted so that 1 mm. on the original film represents about 0.0007 sec.

In all cases the curve I represents a pure I.R. drop; it is the I.R. drop through the solution and may be measured by the potentiometer while the polarizing current is flowing. The value so measured agrees almost perfectly with the value calculated from a comparison of the drop in the I curve with the calibrated film. The curve A represents the decay of anode potential. It is to be noted that this decay is slow throughout its entire length, giving no indication of an I.R. drop. Curve Ai is the sum of the potentials represented by A and I, and shows the nature of a potential decay curve that does contain, also, a potential due to an I.R. drop. These curves indicate that the overvoltages, both at anode and cathode,

are very small at these current densities, and that there is no I.R. drop through any kind of film at the electrodes.

Curves for smooth platinum are shown in figures 7 and 8. In agreement with previous findings in this laboratory, the initial overvoltage decay for smooth platinum is far more rapid than for platinized platinum. However, in contrast to the earlier work, in which the decay curves for the electrode potentials could not be distinguished from an I.R. drop, it is clearly evident from these figures that the present equipment is capable of making this separation. Both the anode and the cathode potentials, curves A and K respectively, diverge from the vertical line I, which is due

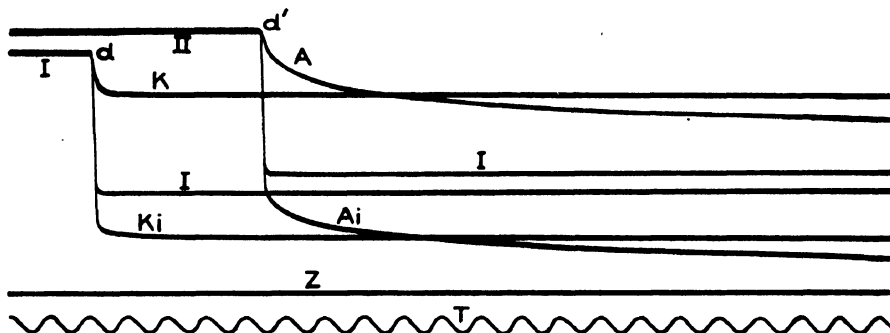


FIG. 8. Overvoltage decay curves for smooth platinum electrodes.
Amplifier system VI

Curve	Potential measured	Value in volts	C. D. in milliamperes
A	Anode vs. anode standard	2.075	7.26
Ai	Anode vs. cathode standard	2.481	7.26
K	Cathode vs. cathode standard	0.162	7.26
Ki	Cathode vs. anode standard	0.569	7.26
I	Anode standard vs. cathode standard	0.406	7.26
Z	Zero line of vibrator		

to a pure I.R. drop, from the instant the polarizing current is interrupted. This appears to be conclusive evidence for the non-existence of a potential drop due to transfer resistance or any other resistance even at smooth platinum electrodes. These curves show, also, that the initial rate of overvoltage decay for smooth platinum electrodes is slower at the anode than at the cathode.

When comparing the curves in different figures one must be sure to take into account the particular amplification system used. For the comparison factors see table 1.

The behavior of a palladium electrode during electrolysis differs from platinum in many respects. When a fresh palladium electrode, or one which has been used previously as an anode, is polarized cathodically,

electrolysis must be continued during several hours at a current density of several milliamperes before a visible evolution of hydrogen occurs. With the appearance of hydrogen bubbles the cathode potential rises rapidly to a definite value. After an electrode has been used as a cathode it may be removed from the electrolyte for several hours, and if it is again polarized cathodically hydrogen evolution will begin almost immediately, followed by a rapid rise of potential to the normal overvoltage value.

Overvoltage decay curves for a palladium cathode at several current densities are shown in figure 9. These curves drop very rapidly to what appears to be a constant value, which would be explained if a compound of hydrogen were formed at the palladium cathode. It should be remembered

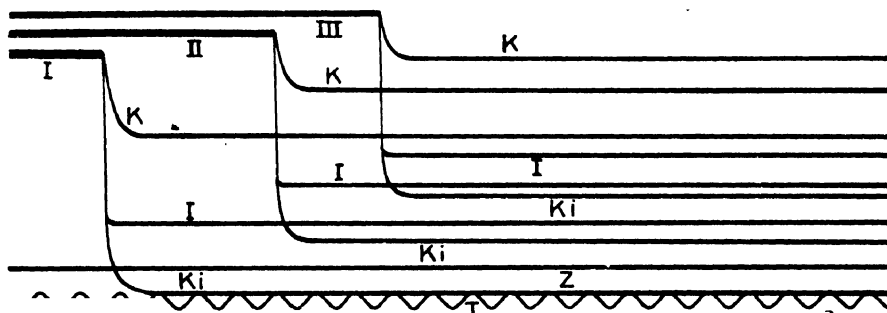


FIG. 9. Overvoltage decay curves for a palladium cathode at several current densities

<i>Curve</i>	<i>Potential measured</i>	<i>Group I, system I</i>	<i>Group II, system II</i>	<i>Group III, system III</i>
K	Cathode vs. cathode standard	0.046 v.	0.062 v.	0.081 v.
Ki	Cathode vs. anode standard	0.086 v.	0.143 v.	0.232 v.
I	Cathode standard vs. anode standard	0.040 v.	0.082 v.	0.152 v.
Current density		1.0 ma.	2.08 ma.	3.85 ma.
Z	Zero line of sensitive vibrator			
T	120-cycle timing curve			

that these experiments were designed to study the character of the extremely rapid initial drop of potential at the beginning of the discharge and that, therefore, the photographs were taken at high speeds. If a low speed were used a curve having a definite but small downward slope extending to the normal hydrogen value might be obtained. This matter is under investigation at the present time.

A comparison of the K curves with the vertical portion of the I curves proves that no surface resistance exists at the cathode-electrolyte interface.

The behavior of a palladium anode during electrolysis is similar to that of a cathode. A new electrode, or one which has been used previously as a cathode, requires several hours before visible oxygen bubbles appear. Prolonged electrolysis results in a tarnishing of the surface.

Curves representing the anodic overvoltage decay for palladium are given in figure 10. The anode curves, A, slope gradually downward throughout the time of the exposure in contrast with corresponding curves for the cathode, where a rapid initial drop is followed by a very slow change. The overvoltage at the anode is much larger than at the cathode.

Curves for gold as cathode are represented in figure 11 and as anode in figure 12. Again the anode overvoltage is much greater than the cathode. Upon prolonged electrolysis the gold anode is tarnished to a dull chocolate color.

The cathode decay curves for silver are shown in figure 13. Reproducible curves could not be obtained for silver as anode.

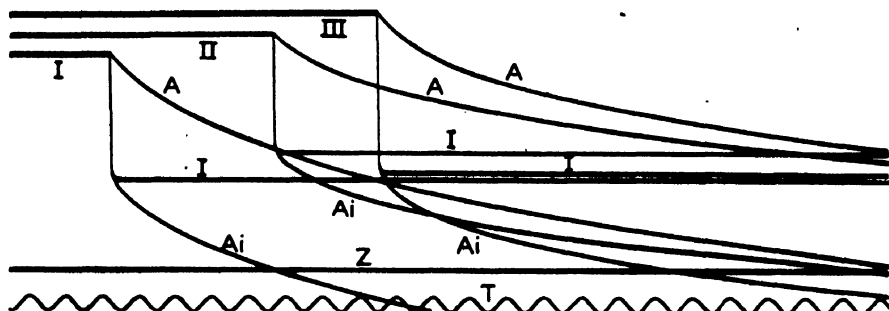


FIG. 10. Overvoltage decay curves for a palladium anode

Curve	Potential measured	Group I, system II	Group II, system III	Group III, system III
A	Anode vs. anode standard	1.842 v.	1.864 v.	1.873 v.
Ai	Anode vs. cathode standard	1.909 v.	1.991 v.	2.044 v.
I	Anode standard vs. cathode standard	0.068 v.	0.126 v.	0.171 v.
Current density		1.70 ma.	3.18 ma.	4.37 ma.
Z	Zero line of sensitive vibrator			
T	120-cycle timing curve			

Zinc under ordinary conditions displaces hydrogen from 2 *N* sulfuric acid solution. Preliminary cathodic polarization of pure zinc, followed by buffing with clean cotton, results in a smooth surface which is passive. In most cases an electrode treated in this manner may be used as a cathode for hours without showing any tendency toward solution. Overvoltage curves for zinc as cathode are given in figure 14. Zinc shows an extremely rapid initial drop and then remains nearly constant.

The curves for cadmium are given in figure 15. These curves show that cadmium has an unusually high overvoltage, a large part of which disappears very rapidly.

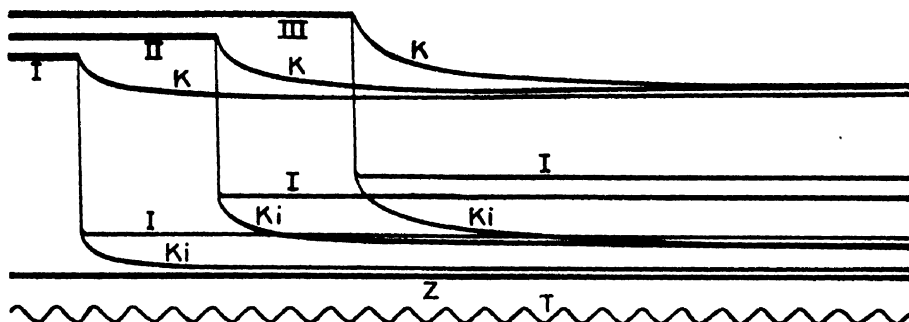


FIG. 11. Overvoltage decay curves for gold cathode

Curve	Potential measured	Group I, system VI	Group II, system V	Group III, system IV
K	Cathode vs. cathode standard	0.491 v.	0.485 v.	0.484 v.
Ki	Cathode vs. anode standard	1.003 v.	0.831 v.	0.747 v.
I	Cathode standard vs. anode standard	0.512 v.	0.346 v.	0.263 v.
Current density		12.26 ma.	8.87 ma.	6.75 ma.

Z Zero line of sensitive vibrator
 T 120-cycle timing curve

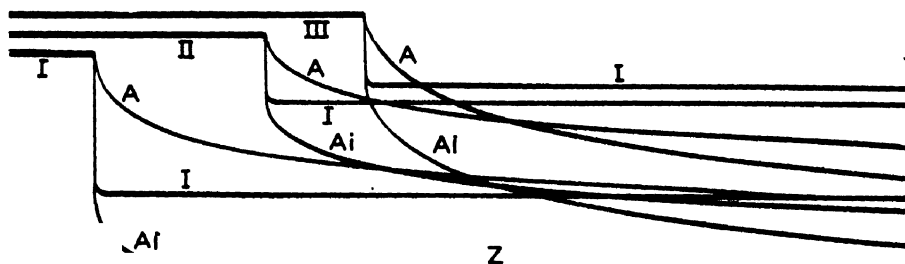


FIG. 12. Overvoltage decay curves for gold anode

Curve	Potential measured	Group I, system III	Group II, system III	Group III, system II
A	Anode vs. anode standard	2.046 v.	2.027 v.	2.010 v.
Ai	Anode vs. cathode standard	2.196 v.	2.096 v.	2.044 v.
I	Anode standard vs. cathode standard	0.150 v.	0.069 v.	0.034 v.
Current density		2.9 ma.	1.38 ma.	0.73 ma.

Z Zero line of sensitive vibrator
 T 120-cycle timing curve

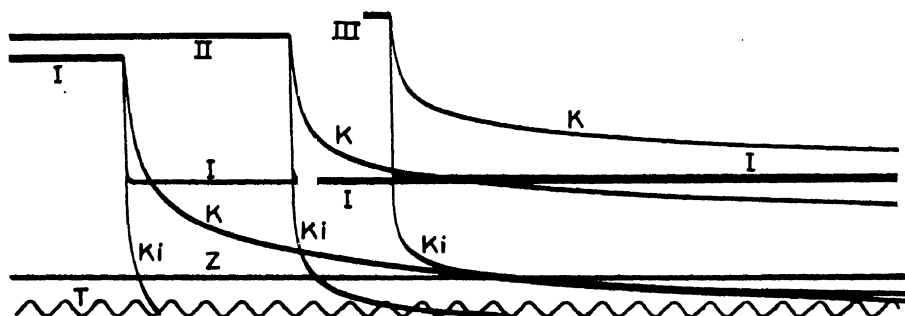


FIG. 13. Overvoltage decay curves for silver cathode

Curve	Potential measured	Group I, system III	Group II, system IV	Group III, system V
K	Cathode vs. cathode standard	0.480 v.	0.506 v.	0.520 v.
Ki	Cathode vs. anode standard	0.609 v.	0.749 v.	0.873 v.
I	Cathode standard vs. anode standard	0.128 v.	0.243 v.	0.348 v.
Current density		2.40 ma.	4.4 ma.	6.5 ma.

Z Zero line of sensitive vibrator
T 120-cycle timing curve

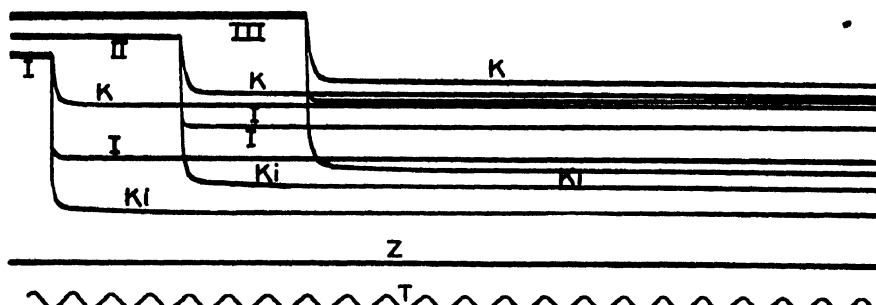


FIG. 14. Overvoltage decay curves for zinc cathode

Curve	Potential measured	Group I, system VI	Group II, system V	Group III, system IV
K	Cathode vs. cathode standard	0.985 v.	0.942 v.	0.939 v.
Ki	Cathode vs. anode standard	1.302 v.	1.150 v.	1.086 v.
I	Cathode standard vs. anode standard	0.317 v.	0.205 v.	0.147 v.
Current density		7.15 ma.	4.62 ma.	3.33 ma.

Z Zero line of sensitive vibrator
T 120-cycle timing curve

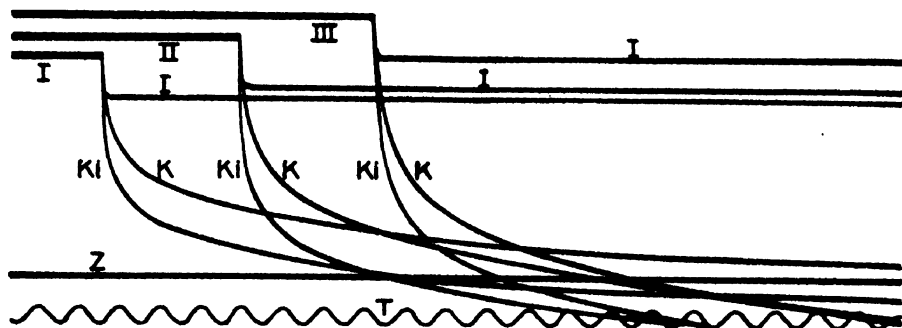


FIG. 15. Overvoltage decay curves for cadmium cathode

Curve	Potential measured	Group I, system VI	Group II, system V	Group III, system IV
K	Cathode vs. cathode standard	1.117 v.	1.116 v.	1.078 v.
Ki	Cathode vs. anode standard	1.234 v.	1.210 v.	1.149 v.
I	Cathode standard vs. anode standard	0.117 v.	0.094 v.	0.071 v.
Current density		3.0 ma.	2.42 ma.	1.79 ma.

Z Zero line of sensitive vibrator

T 120-cycle timing curve

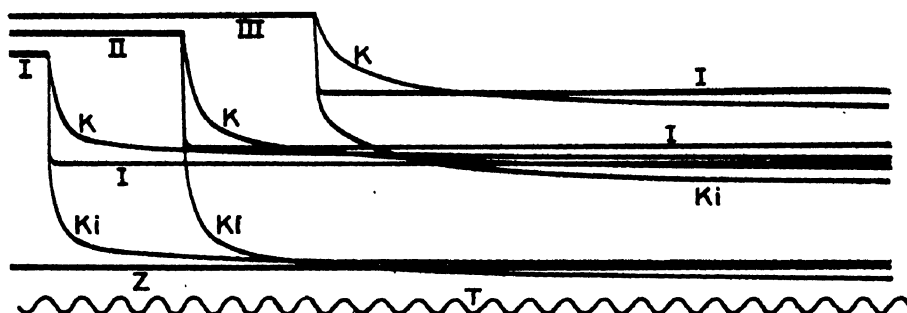


FIG. 16. Overvoltage decay curves for antimony cathode

Curve	Potential measured	Group I, system III	Group II, system II	Group III, system I
K	Cathode vs. cathode standard	0.615 v.	0.579 v.	0.525 v.
Ki	Cathode vs. anode standard	0.731 v.	0.641 v.	0.544 v.
I	Cathode standard vs. anode standard	0.116 v.	0.062 v.	0.019 v.
Current density		2.94 ma.	1.55 ma.	0.46 ma.

Z Zero line of sensitive vibrator

T 120-cycle timing curve

Cathode curves for antimony and nickel are shown in figures 16 and 17, respectively.

In every case studied the decay curves diverge from the corresponding I.R. drop curves immediately. These facts show conclusively that no part of the overvoltage decay is as rapid as an I.R. drop and, therefore, the possibility of the inclusion of a potential drop through some kind of resistance at the electrode solution interface in the measured electrode potential is excluded.

From a careful analysis of the cathode decay curves presented here and many others not included in this paper, it appears probable that at least

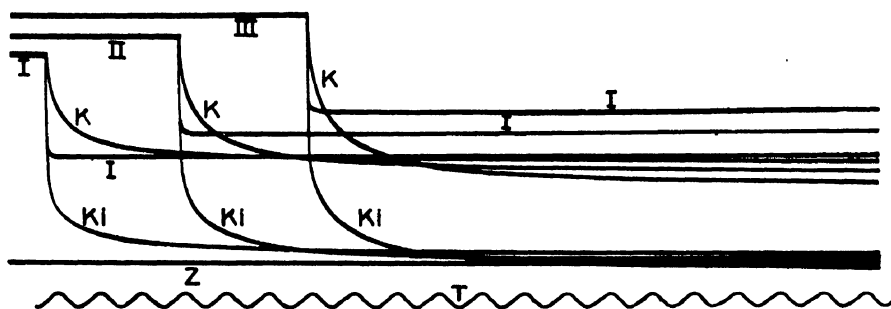


FIG. 17. Overvoltage decay curves for nickel cathode

Curve		Group I, system VI	Group II, system V	Group III, system IV
K	Cathode vs. cathode standard	0.520 v.	0.509 v.	0.494 v.
Ki	Cathode vs. anode standard	0.817 v.	0.723 v.	0.656 v.
I	Cathode standard vs. anode standard	0.297 v.	0.214 v.	0.162 v.
Current density		5.72 ma.	4.09 ma.	3.1 ma.
Z	Zero line of sensitive vibrator			
T	120-cycle timing curve			

two different causes are responsible for the total measured overvoltage. The first of these appears as an extremely rapid potential drop which, for most materials studied, is completed in less than 0.01 sec. This extremely rapid initial drop is followed by a slow decay, probably to the value of the normal hydrogen electrode. Only the initial rapid drop and the first portion of the slow decay were investigated in this research; thus it is not possible to arrive at conclusions regarding the later stages of the slow decay.

The value of the total hydrogen overvoltage increases with current density for all the materials used. The value of the initial rapid drop also increases with current density; but the residual overvoltage, i.e., the difference between the total overvoltage and that represented by the initial

rapid drop, is nearly constant for a given metal and is independent of current density. This is the first time that such an observation has been noted, because it is the first time that it has been possible to measure the very rapid initial overvoltage drop. Values for the initial overvoltage, the residual overvoltage, and total overvoltage are collected in table 2. This table contains data, also, from several curves not included in this paper. The variation of initial overvoltage with current density is evident from the values in column 3, and the constancy of residual overvoltage is evident from column 5. Both types of overvoltage depend to a pronounced degree upon the material used as electrode.

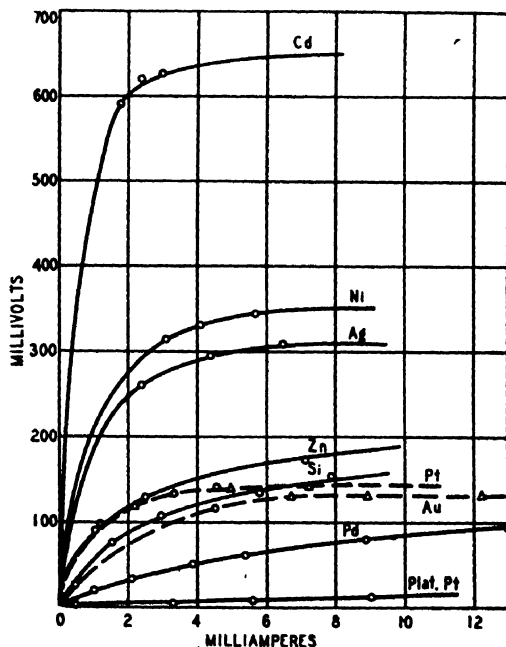


FIG. 18. Initial rapid overvoltage drop vs. current density

Curves showing the relation between current density and the overvoltage corresponding to the early rapid drop, data for which are contained in columns 1 and 3 of table 2, are given in figure 18. It is assumed that this type of hydrogen overvoltage is zero at zero current density and thus all the curves pass through the origin. These curves show considerable regularity, but no special significance is attached to them by the authors.

It is interesting to consider the data in this paper in the light of modern theories of overvoltage. The most interesting recent experimental work has been done by Bowden and coworkers. Bowden based his theory of overvoltage upon results obtained within the range of current densities from 10^{-8} to 10^{-3} amp. per square centimeter. Using a mercury electrode and

TABLE 2
Summary of hydrogen overvoltage values

CATHODE	(1) CURRENT DENSITY	(2) TOTAL OVER- VOLTAGE	(3) INITIAL OVERVOLT- AGE DROP	(4) PER CENT OF TOTAL	(5) RESIDUAL OVER- VOLTAGE
	<i>ma.</i>	<i>mv.</i>	<i>mv.</i>		<i>mv.</i>
Platinized platinum.....	0.485	8	0	20	8
	3.32	29	4		25
	5.58	38	7		31
	9.05	43	13		30
Smooth platinum.....	2.20	140	120	86	20
	5.02	162	138		24
	7.26	162	142		20
Palladium.....	1.00	46	20	65	26
	2.08	62	33		29
	3.85	81	52		29
	5.43	93	61		32
	8.94	111	79		32
	13.54	127	95		32
Gold.....	6.75	484	128	26	356
	8.87	485	126		359
	12.26	491	131		360
Silver*.....	2.40	480	260	57	220
	4.40	506	295		210
	6.50	520	310		210
Zinc.....	1.05	897	92	14	805
	1.24	901	97		804
	2.84	939	127		812
	3.33	939	129		810
	4.62	942	140		802
	7.15	985	175		810
Cadmium*.....	1.79	1078	590	55	488
	2.42	1116	620		496
	3.00	1117	625		492
Antimony.....	0.460	525	27	17	498
	1.55	579	75		504
	2.95	615	105		510
	4.55	617	117		500
	5.80	632	135		497
	7.88	652	154		498
Nickel.....	3.10	494	315	65	179
	4.09	509	332		177
	5.72	520	346		174

* Curves still have a distinct slope. Values correspond to a time one-sixth of a second after the interruption of the charging circuit.

a current density of 0.04 ma. he reported that there was no rapid initial drop in the cathode decay curve, but only a gradual drop from the moment the charging current was interrupted. In the light of the data presented in table 2 of the present paper this would be expected, since, at the current density used, probably only the type of overvoltage included in column 5 is effective.

In the same paper Bowden found that at current densities between 10^{-8} and 10^{-4} amp., $n = a + b \log i$, where n is the overvoltage, i the current density, and a and b are constants. Within this current density range, b was found to equal 0.120. At higher current densities, roughly 10^{-4} to 10^{-3} amp., the relation became $n = a + 2b \log i$. The data in table 2 offer a qualitative explanation for these observations. Within the range of low current densities, where the relation is $n = a + b \log i$, only the residual type of overvoltage corresponding to values in column 5 is effective; in the higher range of current densities both types of overvoltage represented by columns 3 and 5 are increasing simultaneously, giving a constant for b about twice the former. This explanation is supported by the fact that the portion of the cathode decay curve between the rapid initial drop and the subsequent slow decay shows a gradual change in slope, as would be expected if two potential drops, one rapid and one slow, were superimposed. The type of overvoltage represented by the values in column 3 appears at current densities above about 10^{-4} amp., and therefore was not studied or recognized by Bowden. At these high current densities the logarithmic relation does not hold, the overvoltage changing less rapidly with current density.

Bowden and Rideal assumed a difference between the apparent and "accessible area" of a metal surface to explain the difference in the quantities of electricity required to cause an equal increase in overvoltage at different metal electrodes having the same apparent area. For instance, they found that the "accessible area" of a platinized platinum electrode was as much as 2000 times the apparent or regularly measured area. Yet, in developing their relations between overvoltage and current density they used the apparent area, as have all previous workers in attempts to develop such relationships. If there is the great variation between the actual, effective, or accessible area and the geometric area, which is the only one that can be accurately measured, it appears to the authors that relationships such as above expressed between overvoltage and the geometric area should have no significance.

Probably the most plausible theory of overvoltage, based upon experiment, is the dipole theory proposed by Bowden. It was developed, however, with the aid of data obtained at current densities below those employed in this research. It is not surprising, therefore, that the data

submitted here do not fit well into his theory. They do show conclusively that his theory as postulated cannot be complete.

Probably the most promising theory of overvoltage from a theoretical point of view is based upon the recent considerations of Butler, Gurny, Fowler, and their associates, in which attempts are made to interpret electrode phenomena including overvoltage by the application of quantum mechanics.

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A PHYSICOCHEMICAL STUDY OF BLOOD SERA. II

ANALYSES OF FIVE HUNDRED CASES

JOSÉ ZOZAYA

Gladwyne Research Laboratories, Gladwyne, Pennsylvania

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The change in the total protein of the blood serum under different conditions has been studied by Peters, Eisenman, and Bulger (18) in normal individuals and under miscellaneous conditions. Rowe (20) studied the effect of venous stasis on the proteins of human serum. The same author (21) studied the effect of muscular work, diet, and hemolysis on the serum proteins. Holman, Mahoney, and Whipple (11) have studied the change in plasma proteins caused by starvation, diet, and intravenous injection of plasma proteins. Bruckman, D'Esopo, and Peters (1) have reported the same changes in malnutrition. Wiener and Wiener (27) have made a general study of the plasma proteins in many conditions. Marriott (15) has observed and reviewed the literature of blood changes in anhydremia. Peters and Van Slyke (19) have discussed and further reviewed the general literature on the subject.

The author (29) has described a physicochemical method for the study of blood serum and has suggested the direct application of that method in differentiating various pathological conditions. This differentiation can be made with exclusive physicochemical data; definite groups can be formed. The present paper includes the analyses and grouping of five hundred consecutive cases from over fifteen hundred mental and nervous cases that have been studied at the Gladwyne Research Laboratories.

The normal amount of total protein in human serum or plasma has been studied by many investigators. Salvesen (22), Linder, Lundsgaard, and Van Slyke (14), Bruckman, D'Esopo, and Peters (1) are among those who have reported data comparable to ours, for they have used the method of Howe (12) for the fractionation of the albumin and globulin and determined the nitrogen by the Kjeldahl method. The average of all these determinations gives 7 per cent total protein, 4.39 per cent albumin, and 2.61 per cent globulin, including fibrinogen. The figures which we have used as our normal average are those of Handovsky (8), which are similar to those obtained by ourselves in normal average people, namely 7.00 per cent total protein, 4.15 per cent albumin, 1.60 per cent pseudoglobulin, and 1.25 per cent euglobulin, making albumin 60.0 per cent of the total protein, pseudoglobulin 22 per cent, and euglobulin 18 per cent.

The grouping of our cases was based on the deviation of a normal average distribution of the proteins and total amount of protein. Group II contain those cases with a euglobulin per cent of 21 or more; group III, those with a pseudoglobulin per cent of 25 or over; group IV, those cases with an albumin percentage of 65 or over; group I, those cases that did not fall in any of the other groups and which imply an average normal distribution of the proteins with a plus or minus of 3 per cent for the euglobulin and pseudoglobulin and of 5 per cent for the albumin. We have further subdivided each group according to the amount of total protein in each case. In subgroups A we considered the cases with a total protein between 6.70 per cent and 7.49 per cent as a normal average amount; in subgroups B, cases with a total protein higher than 7.49 per cent; and in subgroups C, cases with a total protein lower than 6.70 per cent. This

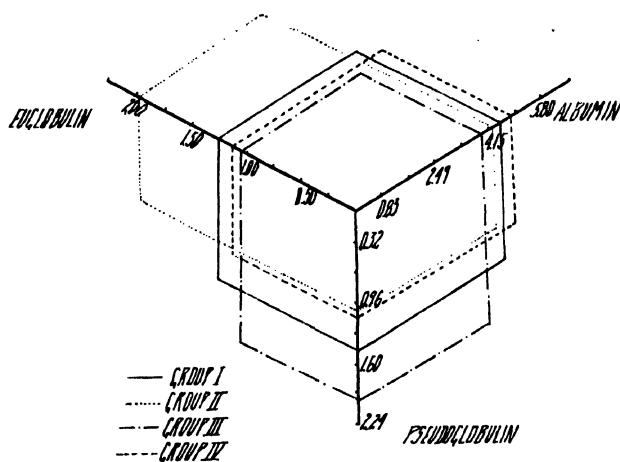


FIG. 1. Chemical chart of the averages of groups I, II, III, and IV

selection has been arbitrary, but seems logical, considering the normal average variations that we have observed.

In figure 1 we have plotted in a three-dimensional diagram the chemical distribution of the total average of the different protein fractions in the four main groups. This plotting gives an approximate equilateral cube which shows the average normal distribution.

The quantitative and qualitative mixture of these protein fractions gives different colloidal properties to the serum. These in turn change the general physiology of the organism, especially in its relation to the water interchange between blood and tissues, for there is no doubt that the interstitial fluid is produced from the blood serum. Krogh, Landis, and Turner (13), studying the movement of fluid through the human capillary wall in relation to colloidal osmotic pressure, support the view that there is a gradient of pressure which permits filtration at the arterial

end and reabsorption at the venous end of the capillary, thus producing a continuous circulation of fluid between capillaries and tissues. Direct measurements of capillary pressure and serum colloid osmotic pressures definitely provide the circulation of fluid, which has been anticipated by theoretical considerations. Thus the colloidal osmotic pressure of a serum, which is usually directly proportional to the quantitative and qualitative distribution of the protein fractions of a serum, becomes of direct importance in the study of movement of water between blood and tissues. This subject has been treated in detail by Peters (17).

There also exist changes in the protein fractions and their amounts in immune reactions. There seem to be sufficient data concerning the two fundamental types of immune reactions (28). One type has to do with substances which are essentially active poisons and whose toxicity is neutralized by direct chemical action. To this group belong the antitoxins from bacterial toxins, such as diphtheria, tetanus, botulinus, etc., snake venoms, vegetable toxins, etc. The substances in this group are similar in that, while having a chemical structure more simple than that of a true protein, they resemble more a colloidal aggregate. The protein change that occurs in this form of immunity reaction is a definite increase in the pseudoglobulin fraction, for it is in this fraction of the protein complex that we find the greatest amount of the antitoxic substance. This fact is recognized, for it is used in the concentration of the antitoxins for commercial use.

The other group of immunity reactions consists of those which are concerned with the defense of the body to definite foreign proteins, polysaccharides, or lipid complexes, whether toxic or non-toxic in themselves. To this group belong the whole protoplasmic bodies of bacteria, their different lipid or carbohydrate fractions, animal or vegetable proteins, etc. In this type of immunity reaction we find a definite increase in the euglobulin fraction of the whole plasma protein of the immunized animal, and the majority of the antibodies produced are found in this fraction. This fact is used in the preparation of purified therapeutic bacterial antibodies.

The difference in chemical response in these two types of immunity reactions by these two groups of substances suggests the direct effect of the chemical structure of the antigen on the reaction of the body to the administration of these substances. In the separation of our groups we have taken this fact into consideration; in group II we have included the cases with a euglobulin increase (second group of immunity reactions) and in group III those with a pseudoglobulin increase (first group of immunity reactions).

The chemical difference between the pseudoglobulins and the euglobulins suggested by Chick (4) and confirmed by Sørensen and some

of his coworkers (24) is that euglobulin in serum is a complex material, formed from pseudoglobulin by association with some serum lipid, to the presence of which it owes its phosphorus content.

Hardy and Mellanby (9) made studies many years ago on the solubility of serum globulin in salt solution, and more recently Sørensen (24) did likewise. The last author believes that in the serum itself, as well as in the special globulin fractions prepared from it, the globulins do not occur as mixtures of two or more globulins but as readily dissociable combinations of the same. As a simple and general term for the composition of such a combination the formula $EpPq$ was utilized, where E indicated a euglobulin complex and P a pseudoglobulin complex, and where previously the probable difference between the individual euglobulin and pseudoglobulin complexes was disregarded.

The study of serum as a readily dissociable component system of protein and the differences observed in our cases give us a fundamental physicochemical point of view which is of general practical and theoretical value. Sørensen (24) says that in serum an interaction must be presumed to occur between all the protein systems present, an interaction which may lead to the formation of new systems possibly containing components from albumin systems as well as from globulin systems and perhaps capable, to a limited extent, of giving rise to the formation of systems even larger than those known as albumins and globulins. Not only proteins, which as ampholytes have a particularly marked tendency to mutual interaction, but also to a greater or less extent, dependent on concentration conditions and other circumstances, many of the other substances present in biological liquids must be supposed to be more or less closely knit to the, in all probability, highly hydrated protein systems. The views here advanced apply not only to serum but also to plasma and blood, for the blood corpuscles and other form elements in the blood,—readily dissociable complexes consisting of proteins,—and also, to a greater or less extent, other substances present in the blood have to be taken into account. For these large complexes which condition many of the physical properties of the blood plasma, for example, its great viscosity and its comparatively low colloid osmotic pressure, must be imagined in continuous reversible dissociation, dependent on the ever-changing composition of the blood.

The marked changes in amount of pseudoglobulin and euglobulin in serum give the serum different physicochemical properties. The lipid complex in euglobulin gives this substance marked hydrophilic properties, as Chick (3) has found in the study of the hydration numbers of the different serum fractions, establishing for the euglobulin 5.8 cc. per gram, for pseudoglobulin 3.8 cc. per gram, and for albumin 2.1 cc. per gram. These differences in hydration of the various protein fractions affect their hold-

ing power for water. We are aware of the work of Grollman (7), Sunderman (6), and Greenberg (6), who do not believe that there is any appreciable amount of "bound water" in serum. But we agree with Gortner

TABLE 1

Averages of physicochemical observations of the blood serum in 500 mental and nervous cases

GROUP	NO. OF CASES	PER CENT OF TOTAL CASES	VISCOSITY	SPECIFIC GRAVITY	TOTAL PROTEIN	ALBUMIN	PSEUDOGLOBULIN	EUGLOBULIN	ALBUMIN	PSEUDOGLOBULIN	EUGLOBULIN	BOUND WATER	FREE WATER	TOTAL WATER	OSMOTIC PRESSURE	ALBUMIN GLOBULIN
I	94	17.8	1.70	1.0272	7.05	4.38	1.42	1.25	62.1	20.1	17.8	21.8	73.7	95.5	29.6	1.64
I A	58	11.0	1.70	1.0273	7.07	4.38	1.41	1.28	61.9	20.0	18.1	22.0	72.4	94.4	29.7	1.62
I B	14	2.6	1.81	1.0284	7.89	4.88	1.50	1.51	61.8	19.0	19.2	24.7	70.0	94.7	23.0	1.62
I C	22	4.1	1.67	1.0266	6.55	4.02	1.29	1.24	61.3	19.7	19.0	20.5	75.4	95.9	27.3	1.59
II	231	43.7	1.74	1.0276	7.24	4.22	1.08	1.94	58.2	14.9	26.9	24.2	71.1	95.3	28.8	1.39
II A	104	19.7	1.72	1.0274	7.12	4.22	1.07	1.83	59.2	15.0	25.8	23.5	71.9	95.4	28.6	1.45
II B	85	17.0	1.81	1.0283	7.94	4.37	1.18	2.39	55.0	14.8	30.8	27.5	67.2	94.7	30.5	1.22
II C	42	8.0	1.66	1.0266	6.36	3.72	0.93	1.71	58.1	14.6	27.3	21.3	74.8	96.1	25.3	1.41
III	48	9.1	1.72	1.0276	6.81	3.78	1.99	1.0	55.5	28.9	15.6	21.5	74.2	95.7	27.5	1.24
III A	26	4.9	1.72	1.0278	7.04	3.92	2.12	1.00	55.7	30.1	14.2	22.1	72.4	94.5	23.2	1.25
III B	2	0.3	1.80	1.0285	7.80	3.67	2.04	2.08	47.0	26.1	26.9	27.5	67.3	94.8	27.6	0.89
III C	20	3.8	1.72	1.0266	6.37	3.61	1.83	0.93	56.6	28.7	14.7	19.9	76.2	96.1	26.1	1.31
IV	155	29.4	1.68	1.0273	7.00	4.82	1.08	1.10	69.0	15.4	15.6	20.6	74.9	95.5	30.9	2.21
IV A	83	15.7	1.67	1.0273	7.07	4.87	1.09	1.11	68.9	15.4	15.7	20.7	74.7	95.4	31.3	2.21
IV B	28	5.3	1.73	1.0283	7.79	5.24	1.06	1.49	67.2	13.6	19.2	23.7	71.1	94.8	33.7	2.05
IV C	44	8.3	1.67	1.0270	6.40	4.48	1.04	0.88	70.0	16.2	13.8	18.4	77.7	96.1	28.7	2.33
Total	528	100.0	1.71	1.0278	7.09	4.38	1.20	1.51	61.7	16.9	21.4	22.5	74.0	96.5	29.4	1.61

Group I: Distribution of protein fractions average.

Group II: Percentage of euglobulin 21 or more.

Group III: Percentage of pseudoglobulin 25 or more.

Group IV: Percentage of albumin 65 or more.

Subgroup A: Total protein between 6.70 and 7.50.

Subgroup B: Total protein higher than 7.49.

Subgroup C: Total protein lower than 6.70.

(5) and Bull (2), who point out that the concept of "bound water" has a substantial theoretical basis, and it is with this viewpoint that we have used the term here.

METHODS

The methods used in this work are the same as those described in our previous work (29). The mean average for each observation in each group is shown in table 1.

PHYSICOCHEMICAL CHARACTERISTICS OF THE DIFFERENT GROUPS

The physicochemical characteristics of the four main groups can be observed from the average figures for each group.

Group I, the average normal group, can be used as a comparison for the other three groups. In group I we get the general average of the average normal distribution of the protein fractions, as seen in figure 2, where the three-dimensional diagram of each of the subgroups shows a cube with its sides fairly equal. Subgroup A appears, as expected, midway between subgroups B and C. The general physicochemical characteristics

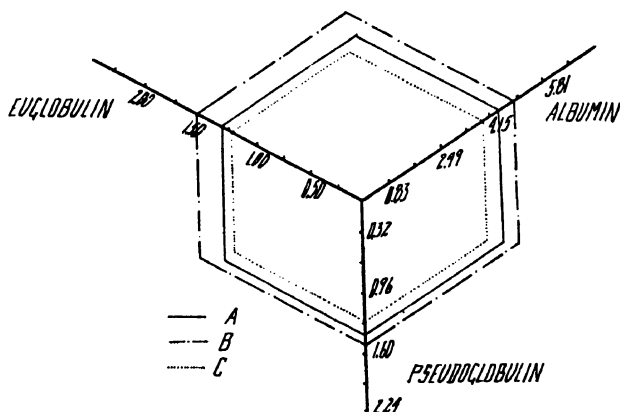


FIG. 2. Chemical chart of subgroups I A, I B, and I C

of this subgroup are those which are typical of a normal serum with, the variations expected due to dilution of the total blood. For example, we find in subgroup B a more concentrated serum than in subgroup C. The concentration of the blood usually occurs through some physiological process, such as anhydremia, malnutrition, etc. The variation of "free water" in each of these subgroups is of interest. The difference between subgroups B and C is 5 cc. of "free water" in 100 cc. of serum. We take subgroup A as our standard of comparison, for it shows the general averages found among normal persons.

In group II we find higher viscosity, higher specific gravity, higher total protein, increase in euglobulin per cent, a large amount of "bound water," low "free water," and a low albumin-globulin ratio. This type of colloidal mixture is a more definite hydrophilic one. With this type of protein system is usually associated a certain definite physiology.

To this whole group we have given the name "hyper-reactive." This hyper-reaction, which is based on the increase of the euglobulin fraction, suggests an immunity response to a stimulation of some sort. This response is similar to that found in immunity reactions produced by a protein complex. The larger the amount of euglobulin in the serum, the more phospholipins there are bound to the protein fraction. This union alters the general physicochemical properties of the serum. With this kind of protein complex (euglobulin), we find changes in the water interchange between the blood and tissues, thus disturbing one of the most important of body functions. We find the same condition in subgroups B and C, to a more marked degree in subgroup B, and to a less extent in subgroup C. The main difference between these two subgroups is in the amount of total protein, which suggests in the last group (C) a definite

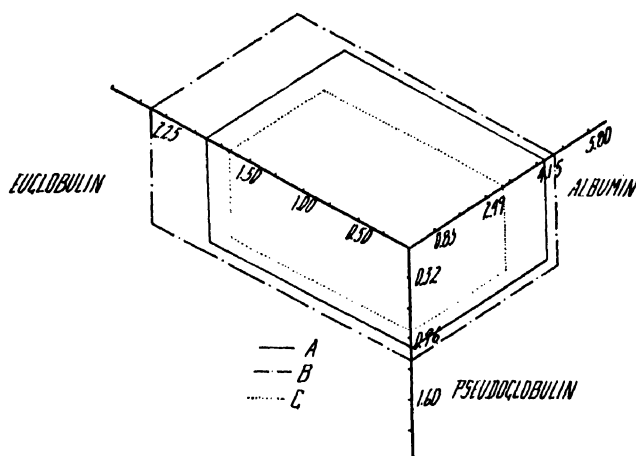


FIG. 3. Chemical chart of subgroups II A, II B, and II C

dilution, as is indicated in changes in specific gravity and viscosity. For the chemical-fractional plotting of the three subdivisions of group II, see figure 3.

Group III is characterized by an increase of above 25 per cent in the pseudoglobulin fraction in relation to the total protein. To this group belong the general reactions that from immunological experience are expected to come from stimulation by toxic substances of a simple chemical composition. These substances may come from any by-product of digestion (absorption through the intestine), from some substance that is not properly assimilated by the liver (as we often find the pseudoglobulin fraction markedly increased in diseases of the liver), or from any other substance which is absorbed and has the characteristics mentioned above.

In subgroup B we have only two cases out of the five hundred. In these two cases there is an increase in the pseudoglobulin fraction as well

as an increase in the euglobulin fraction. This double increase makes the colloidal properties of this subgroup an exceptional one. The specific gravity and the "bound water" are high, while the "free water" is low. From the immunological point of view this shows a double reaction, which suggests a definite liver involvement with a probable generalized reaction to an infection. The low albumin-globulin ratio is typical of this subgroup.

Subgroup C has definite characteristics: low total protein, low "bound water," low specific gravity, and high "free water." This suggests a marked dilution of the blood. For the chemical plotting of the subdivisions of group III, see figure 4.

Group IV, the high albumin percentage group, is of general interest because of the low pseudoglobulin and euglobulin in the mixture. With

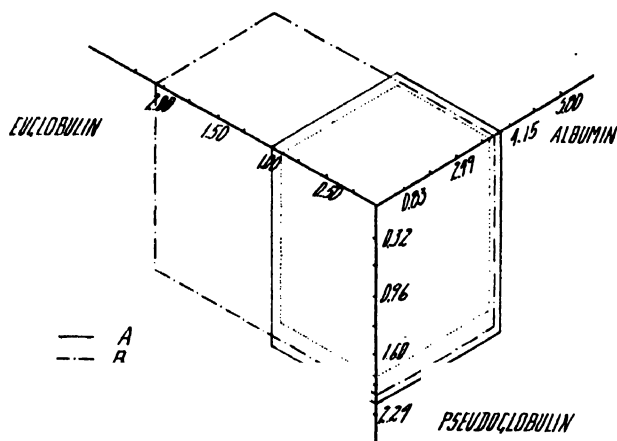


FIG. 4. Chemical chart of subgroups III A, III B, and III C

a preponderance of the albumin fraction, we expect this group to be proportionately less hydrophilic than the others, so we find high "free water" and a high osmotic pressure. Chemically it is the direct opposite to group II, and, owing to the low concentration of the pseudoglobulin and euglobulin fractions, we have termed it, from an immunological point of view, the "non-reactive" group. It seems that the individuals in this group do not react immunologically. Probably the reticulo-endothelial system in this group of cases is blocked or markedly deficient.

The chemical distribution of the subgroups is seen in figure 5.

Subgroup B has the general characteristics of the group except that it has a high total protein. Subgroup C is directly opposite to subgroup B. It is between these two opposite groups that we find the most marked differences. The main characteristics of this subgroup (IV C) are a low total protein, low "bound water," high "free water," high albumin-globulin ratio, and a relatively high osmotic pressure.

In order to understand further the physicochemical differences between the various groups, we study the relation between specific gravity and the total protein per cent. The results are shown in figure 6. The total average of each group falls lowest for group I and highest for group III. Groups I and II follow a straight line. Groups III and IV are askew,

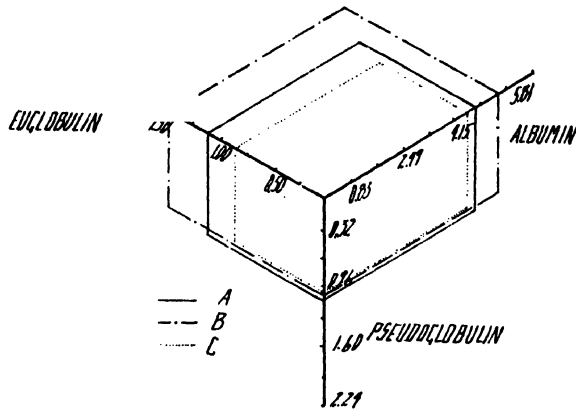


FIG. 5. Chemical chart of subgroups IV A, IV B, and IV C

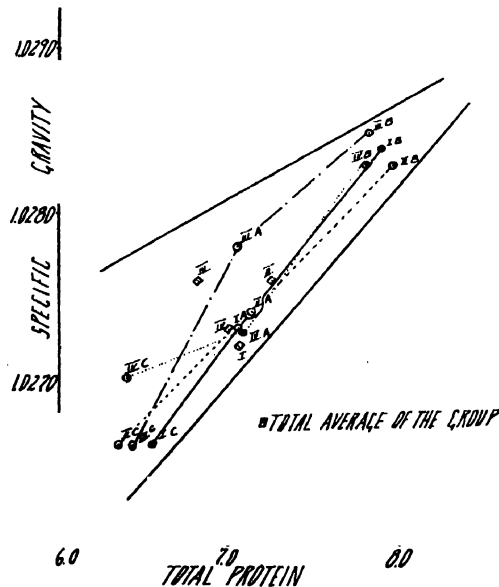


FIG. 6. Relation between specific gravity and total protein in all the groups

subgroup III A being out of line as well as subgroup IV C. The corresponding subgroups of all the different groups fall within reasonable expectation.

The study of these cases in groups shows a different relation between specific gravity and total protein, for in our previous work (29) we found

the index of correlation between these two measurements to be 0.282 ± 0.062 . From this chart we can assume that in the present distribution we would expect a much higher correlation when the cases are grouped by chemical characteristics. The heavy solid lines are drawn to show the apparent band of distribution, expecting greater discrepancies between specific gravity and total protein in the cases of lower total protein with increased albumin percentage than in the other groups.

In studying further the relation of specific gravity to some of our other measurements or calculations, we used "bound water" as the other relation, because by the method we use in calculating it we get a quantitative-qualitative evaluation of the protein fractions in the particular mixture.

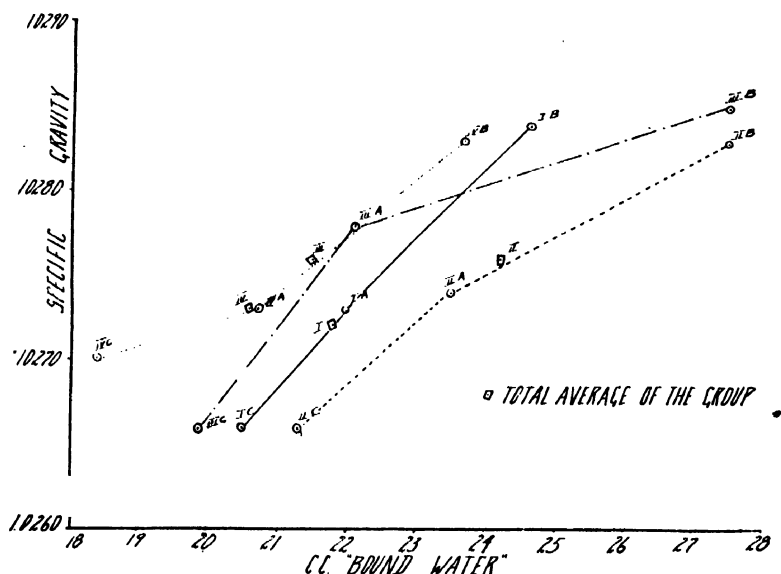


FIG. 7. Relation between "bound water" and specific gravity in all the groups

Using this value we could study the effect of this difference and specific gravity. Our results are plotted in figure 7.

As expected from the theory, group I is in the middle, group II below (plus euglobulin), and group IV above (plus albumin). Group III shows a different trend, but group III B returns to line. (In group III B we have only two cases, which we believe are definitely abnormal.) The total average of each group falls close within the line of general trend.

Chick's studies (3) on the volume occupied by 1 g. in solution of the different protein fractions used Hatschek's (10) formula, modified to apply to emulsoids of the protein type. The formula as given by Chick is as follows:

$$= \left(\frac{n}{n-1} \right)^3, \quad A' = \frac{100}{d \times c}, \quad \frac{A'}{A} = \frac{v}{c}$$

where n = viscosity of the protein solution, d = specific gravity of the protein solution, and c = concentration of the protein in per cent. The relation A'/A is the expression of the volume occupied by unit weight of the dissolved substance.

We are aware that this formula of Hatschek's does not directly apply to our systems, because the formula appears to hold true only when the disperse phase occupies more than one-half of the total system. In

TABLE 2

The value of A'/A to express the volume occupied by unit weight of the dissolved substance in each one of the groups

GROUP	c^*	d	n	A	A'	A'/A
I	7.05	1.0272	1.70	14.3	13.8	0.96
A	7.07	1.0273	1.70	14.3	13.7	0.96
B	7.89	1.0284	1.81	12.2	12.3	1.01
C	6.55	1.0266	1.67	15.6	14.8	0.95
II	7.24	1.0276	1.74	12.8	13.4	1.04
A	7.12	1.0274	1.72	13.6	13.6	1.00
B	7.94	1.0283	1.81	11.1	12.2	1.10
C	6.36	1.0266	1.66	15.8	15.3	0.96
III	6.81	1.0276	1.72	13.6	14.3	1.05
A	7.04	1.0278	1.72	13.6	13.8	1.01
B	7.80	1.0285	1.80	11.2	12.4	1.10
C	6.37	1.0266	1.72	13.6	15.3	1.12
IV	7.00	1.0273	1.68	15.0	13.9	0.92
A	7.07	1.0273	1.67	15.6	13.7	0.88
B	7.79	1.0283	1.73	13.3	12.4	0.93
C	6.40	1.0270	1.67	15.6	15.2	0.97

* c = concentration of protein in per cent.

d = density of system.

n = coefficient of viscosity.

A = volume of 100 g. of system

volume of disperse phase ($=v$)

volume of 100 g. of system

A' = weight of dissolved substance ($=c$)

A'/A = volume occupied by 1 g. of dissolved substance ($=v/c$).

greater dilution it is probable that relatively more "bound water" than that indicated by the formula is closely associated with the protein molecule. Nevertheless we thought it of interest to use it here and test its general theory.

In table 2 we find the values of A and A' , and the ratio A'/A , and in figure 8 we show the plotting of these values in relation to cubic centimeters of "bound water" per 100 cc. of serum.

In the study of the figure we note the normal trend of the subgroups in groups I and II and the marked skewness of the curves of the subgroups in groups III and IV. The abnormal point seems to be in both cases in subgroup C. It may well be that the relation A'/A does not hold true in the lower concentration of albumin and pseudoglobulin, for Chick found that in the lower concentrations of the different protein fractions this ratio increased in abnormal proportion as the concentration decreased. Why should albumin and pseudoglobulin in this particular property behave so differently from euglobulin? Probably the "bound water"—"free water" relationship is markedly disturbed, as is also suggested by the specific gravity—total protein relationship. From Chick's work (3) the volume occupied by 1 g. of protein solution in high concentration is for serum

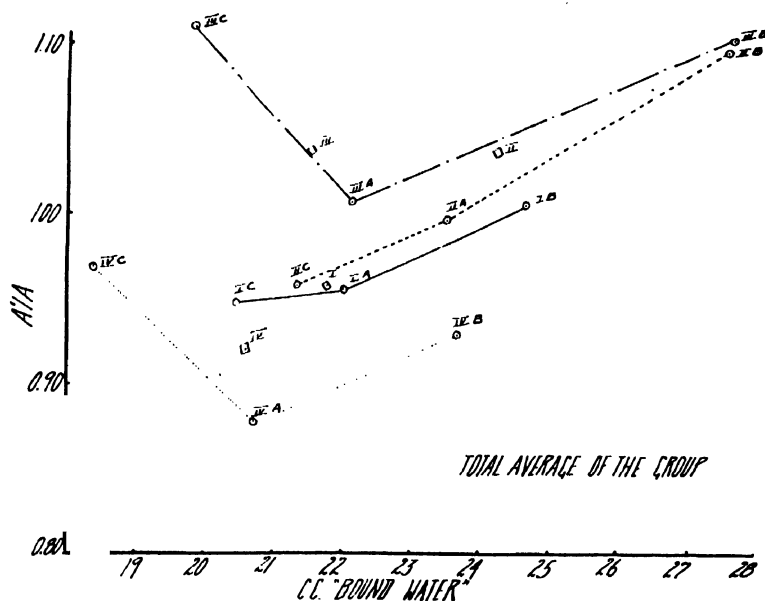


FIG. 8. Relation between A'/A and "bound water" in all the groups

albumin 2.8 cc., for pseudoglobulin 4.5 cc., and for euglobulin 6.5 cc. Therefore, the curve for the different groups as shown in figure 8 follows the general theory, although the concentration is much below the one used by Chick.

Viscosity measurements are of great significance in the study of colloids and any change in these measurements suggests change in the internal colloidal system.

The relation between specific gravity and viscosity has been used as a general estimate of the relation of total protein and the albumin—globulin ratio. In our previous paper (29) we found that the index of correlation between these two measurements was 0.075 ± 0.06 , that is, there was no

correlation. This result was obtained from the ungrouped cases studied then. In figure 9 we have plotted the observations from our different groups. Here the total average of the whole group plots according to the expected theory as far as viscosity is concerned, in which the albuminous group (group IV) has the lowest viscosity for a given concentration, then group I (average mixture), then group III (pseudoglobulin), and the highest is group II (euglobulin). The trend followed by the different subgroups is of interest. As in other observations, the subgroups in groups I and II follow a more or less straight curve, while the low concentrations of total protein in the subgroups of groups III and IV show a marked skewness. From the observed facts we can generalize that groups I and II follow in all of our analyses an expected course, which

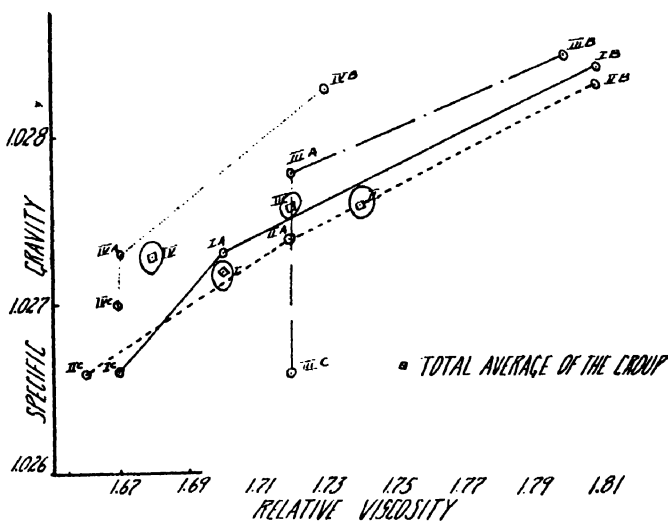


FIG. 9. Relation between specific gravity and relative viscosity

agrees with the theoretical expectations, while in groups III and IV (specifically in subgroup C in both cases) there is always a marked discrepancy as to the expected course of events. In the case of the viscosity-specific gravity relationship we observe that groups III C and IV C give a higher viscosity than expected. In the higher concentrations of protein (subgroups B), all of the groups show a close similarity in their behavior, with the exception of subgroup IV B, which, as we have already stated, has a lower viscosity than the similar subgroups, as might be expected. There is a similar variation in specific gravity in the comparative groups (subgroup IV C excepted), but the viscosity changes follow the laws of protein behavior rather more closely (subgroup III C excepted).

To study further the effect of the chemical constitution of the different groups on viscosity, we selected cubic centimeters of "bound water" as

an indication of relative evaluation of the different protein fractions, as we have done before in figure 8, and we plotted the relation between these two measurements, as shown in figure 10. Here we find the same observation as discussed before, all of the groups behaving according to theory with the exception of subgroups III C and IV C. It is of interest to note that the albuminous group (group IV) comes below group I. Comparing this observation with that found in figure 7, we note that in the relationship of specific gravity to cubic centimeters of "bound water" group IV comes above all the groups, suggesting the high specific gravity in relation to the "bound water"; and in relation to the viscosity, group IV has higher "bound water" than expected. Groups IV A and IV C are simi-

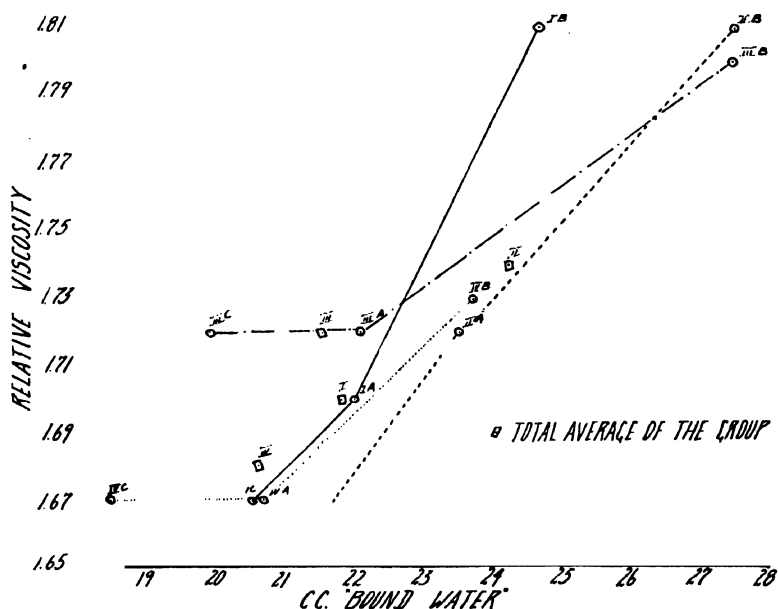


FIG. 10. Relation between relative viscosity and "bound water" in all the groups

lar in viscosity but different in "bound water," the same as in groups III A and III C. We cannot account for this similarity in viscosity except that in the lower dilutions the "bound water" probably increases above our calculation, as shown by Chick in her experiments.

In order to study the relation of specific gravity and the volume occupied by unit weight of the dissolved substances in each of the different groups we plotted our results, which are shown in figure 11. We observe the same phenomena that we observed before, that is, that groups I and II follow the expected relationship between the specific gravity and the ratio A'/A , but that groups III C and IV C show a marked skewness, for the specific gravity does not agree with the volume occupied by the unit of the dissolved proteins. No doubt in these lower concentrations a

new factor enters, which may probably be the proportion in which water enters into the protein molecule or "bound water," for this same skewness is found in figure 8, where the relation between "bound water" and A'/A is shown.

A definite gradient between group II B and group IV C is found, as shown diagrammatically in figure 12, where we have a definite and oppo-

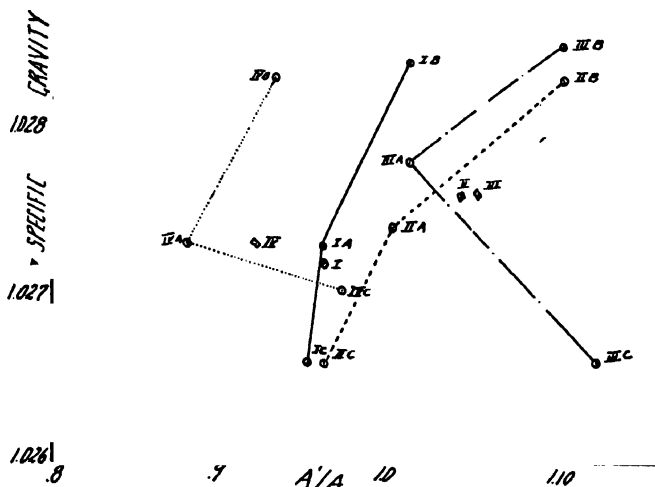


FIG. 11. Relation between A'/A and specific gravity in all the groups

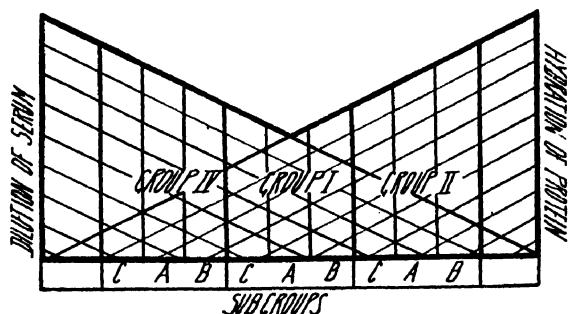


FIG. 12. Graphic representation of the relation between hydration of proteins and dilution of serum

site relation between the hydration of the protein mixture in the serum and its dilution, depending on the chemical composition of the serum. The euglobulin, of the serum proteins, is the one which takes up more water of hydration ("bound water"), while albumin takes up the lowest amount. It would follow that the "free water," or the dilution of the serum, would run opposite to the hydration of the proteins. For one of the most important functions of serum protein resides in the osmotic

attraction for water, and this property of the serum is the most effective agent in maintaining the fluid balance between the blood and intercellular tissues. Smith, Belt, and Whipple (23) have found that intensive and prolonged plasmapheresis results in symptoms resembling those of shock. Stanbury, Warweg, and Amberson (25) have emphasized the importance of the colloidal osmotic pressure of the plasma in maintaining a normal blood volume. Melnick and Cowgill (16) have further shown the important rôle of the serum protein complex as a factor in regulating blood volume. All of the above authors have taken into consideration the amount of total protein and have not given any consideration to the chemical composition of the serum. This factor is probably as important as the amount of total protein, on account of the marked differences in the hydration of the various fractions, as well as in the different volume occupied by each one of the fractions in solution.

The variation in chemical patterns observed in this group of cases is relatively moderate, owing to the selection of our material (nervous and mental cases), but similar studies done with sera from a general hospital would bring out more distinctly the chemical differences found here. As an example, we can refer to marked variations in the total protein between a case of nephrosis (4.0 per cent) and a case of myeloma with a total protein of 14.5 per cent.

SUMMARY

The data resulting from the physicochemical study of the serum of five hundred cases can be put into groups with definite differences which correspond to specific reaction or non-reaction of the organism to well-accepted immunological responses. The differences in the chemical results further suggest differences in the constitution of the individuals.

The chemical groups that we have found behave according to the general laws of protein chemistry, depending upon the chemical constitution.

I wish to thank Dr. S. DeW. Ludlum for his valuable suggestions and help in the development of this work, as well as Dr. V. Alvarez-Hussey and Dr. Robert A. Lichtenthaler for their technical assistance.

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SURFACE-BOUND VERSUS CAPILLARY-CONDENSED WATER IN WOOD¹

ALFRED J. STAMM AND L. A. HANSEN

*Forest Products Laboratory,² Forest Service, U. S. Department of Agriculture,
Madison, Wisconsin*

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It is generally conceded that the water held by cellulose and by wood with a reduction in the equilibrium relative vapor pressure is held either by direct surface molecular forces or by capillary condensation. The extent to which each of these is effective is, however, still controversial. Sheppard and Newsome (6) and Stamm (8) have taken the stand that the inflection point in the sigmoid moisture content–relative vapor pressure curves roughly represents the transition point between surface-bound and capillary-held water, the curve being a combination of an adsorption curve, which tends to become parallel to the relative vapor pressure axis, and a capillary condensation curve, which becomes effective in capillaries just slightly exceeding molecular dimensions and tends to become parallel to the moisture content axis. On this basis the surface-bound water would vary from 3 to 7 per cent for different celluloses and wood, and the capillary-condensed water would amount to 12 to 25 per cent.

Other evidence that the surface-bound water is of this order of magnitude is obtained from the thermodynamic calculations of Stamm and Loughborough (10). The temperature coefficient of the differential heat of swelling–moisture content relationship becomes significant above this moisture content. Presumably the temperature coefficient of capillary condensation is appreciably greater than that of surface adsorption. The entropy change–moisture content relationship further has an inflection point around 6 per cent moisture content, indicating a change in the energy relationship. Extrapolation of the relationship between moisture sorption and temperature at saturated vapor pressures to the critical temperature should give a strictly surface adsorption value. Although this extrapolation cannot be made with any degree of accuracy, available data (10) indicate that the surface-bound water on this basis cannot exceed a few

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² Maintained at Madison, Wisconsin, in cooperation with the University of Wisconsin.

per cent. Predicted values of the surface-bound water of 20 per cent (2) are quite incompatible with these data, as the sorption only slightly exceeds 20 per cent at the experimental temperature of 100°C.

A number of investigators have differentiated between surface-bound water, capillary-held water, and free water on the basis of the first not acting as a solvent for solutes (5). From studies of the effect of salts (7) and sugars (9) upon the shrinking of wood, Stamm concluded that practically all the sorbed water would act as a solvent. These solutes reduced the shrinkage of wood to the oven-dry condition by an amount which would be obtained if the treating solution attained a concentration within the swelling structure practically equal to the bulk concentration and the solute were subsequently deposited within this structure on drying. The accuracy of these measurements is such as to indicate that selective adsorption of water cannot exceed a few per cent.

Barkas (1, 2) has made measurements of the selective adsorption from sugar solutions by wood, from which the air was removed by a special vacuum device to avoid all capillary effects, using an interferometer method to determine the concentration changes. From these data he calculated a minimum value for the bound water for each concentration by considering that sugar is not adsorbed.³ He concluded that approximately 20 per cent of water does not act as a solvent. This value is about three times the estimated value of the surface-bound water from the relative vapor pressure-moisture content curves and the thermal data and is incompatible with measurements of the retardation of shrinkage caused by solutes deposited in the cell wall. It thus seemed desirable to repeat Barkas' measurements with sugar and also to make them with other solutes.

ADSORPTION MEASUREMENTS

The measurements of the selective adsorption of water from aqueous solutions by wood were made with a Hilger-Raleigh gas cell interferometer adapted for use as a liquid cell interferometer in a manner somewhat similar to that used by Ford and McBain (3) and Hall and Jones (4). A water bath was built into the tube zone of the instrument with plate glass windows at the two ends set in adjustable rubber diaphragms. This made possible the perfect alignment of the fringes when the bath was full of water. The cells were made by sealing a piece of 10-mm. Pyrex tubing concentrically into a piece of 40-mm. tubing with an inner seal connection serving for filling (4). Ground Pyrex glass plates were sealed to the parallel ground ends of tubes with silver chloride cement. The cells used ranged

³ What seems to be a typographical error occurs in the derivation of Barkas' equation. The final form of the equation and the calculations made therefrom, however, are correct.

from 7 to 12 cm. in length. This simple construction makes it readily possible to set the cell in such a position that the two beams which give fixed reference fringes and the comparison beam all pass through the solution of lowest refractive index in the large outer tube part of the cell and the adjustable fringe beam passes through the solution of higher index of refraction in the inner tube part of the cell. In all cases investigated the fringe displacement was found to be directly proportional to the concentration.

Sugar pine, in the form of small thin sections about 1 mm. in the fiber direction, was used for the measurements. To insure the removal of all extractives the sections were extracted in a continuous extractor with each of the following solvents for seven days: benzene, methyl alcohol, and water. They were then oven-dried prior to use. Chemically pure sucrose (in the form of rock candy), glycerol, and sodium chloride were used as the solutes. Precautions were taken in the case of the sucrose to perform all operations under sterile conditions. For each measurement 0.3 to 2.5 g. of oven-dry wood was used and enough solution to give ratios of the weight of solution to that of the wood of 20 to 200. A vacuum device, very similar to that of Barkas (2), was used for removing the air from the thin wood sections and for running the solution of known concentration on the wood without loss of solvent. The solutions were allowed to stand in contact with the wood for a minimum time of twenty-four hours at 25°C., after which the equilibrium concentration of the solution was determined with the interferometer, using the original solution as the reference solution.

In the three different solutions used in this investigation, selective adsorption of water took place. Preliminary measurements with other solutions indicate that water is selectively adsorbed from all aqueous solutions that cause a negligible swelling of the wood beyond the water-swollen dimensions, whereas the solute is selectively adsorbed from aqueous solutions that cause an appreciable swelling of the wood beyond water-swollen dimensions. The calculations of the minimum amount of selectively adsorbed water were made by assuming that the adsorption of solute was negligible (2). On this basis the weight of the adsorbed water per gram of dry wood that does not act as a solvent is given by the following equation

$$w_a = \frac{M \Delta C}{X C_2} \quad (1)$$

in which M is the weight of solution in grams in contact with X grams of dry wood, ΔC is the concentration change, and C_2 the equilibrium concentration in grams of solute per gram of solution.

In figure 1 the percentage by weight of water held by the wood that

does not act as a solvent is plotted against the concentration of the solution in equilibrium with the wood in weight per cent. The data for the sugar solutions are very scattered but are in fairly good agreement with the data of Barkas except at low concentrations.

The different solutions, on a weight concentration basis, give different values for w_a . This would be expected, as the capacity of the wood to take water from the different solutions should depend upon the activity of the water in these solutions rather than their concentration. This activity is measured by the relative vapor pressure of water over the solutions. In curve B of figure 2 the percentage of water in the wood not acting as a solvent is plotted against the relative vapor pressure of the

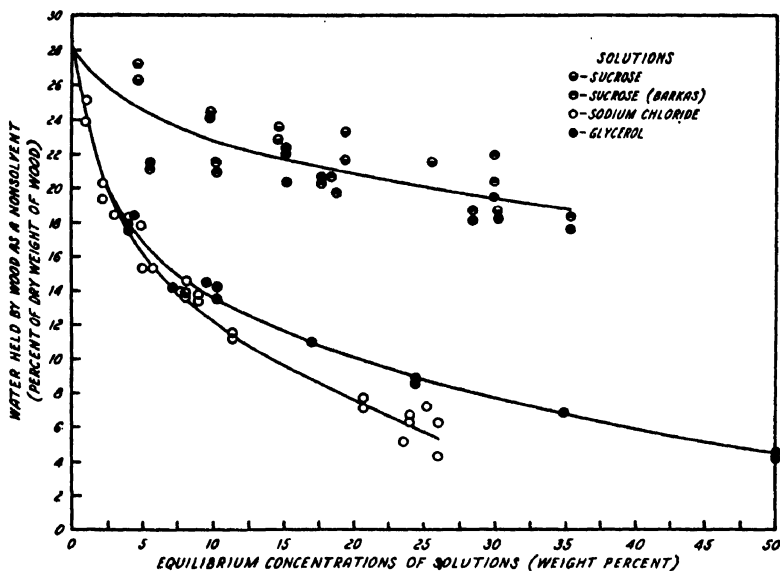


FIG. 1. Selective adsorption of water from aqueous solutions of different concentrations

solution in equilibrium with the wood. In this case all the data can be reasonably well represented by a single curve which seems to be approaching a limiting value of w_a between 3 and 4 per cent; that is, 3 to 4 per cent of water is held by the wood without acting as a solvent when in equilibrium with solutions that depress the equilibrium relative vapor pressure by at least 25 per cent.

DISCUSSION

If the adsorption of water from solution were strictly a monomolecular surface adsorption of a single constituent on a fixed surface, the adsorption would follow a curve such as curve C of figure 2. The experimental variation from this curve might be explained in several different ways:

- (1) The swelling of the wood may increase the internal surface available

for water as adsorption continues. Such an increase in surface, however, should give a-curve similar to curve C except that it does not become parallel to the relative vapor pressure axis.

(2) The solute may be simultaneously adsorbed with the solvent. This would tend to raise curve B and make it more like curve A than curve C.

(3) The force of primary adsorption may extend beyond molecular dimensions, causing polymolecular adsorption at high relative vapor pressures. All recent experimental evidence on innumerable systems, however, indicates that polymolecular adsorption does not take place.

(4) Capillary condensation may not have been completely eliminated, even though the greatest precautions were taken to do so.

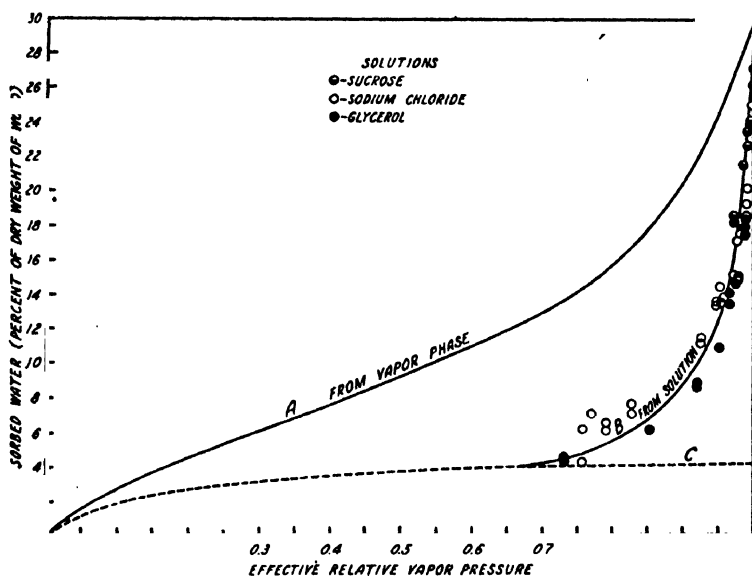


FIG. 2. Water sorbed from the vapor phase and from aqueous solution under different relative vapor pressure conditions.

(5) Complete equilibrium in the distribution of solvent and solute may not have been attained. It has been demonstrated that water is adsorbed from aqueous solutions by wood, followed by diffusion of the solute into the water within the fine structure (7). The amount of water that can be taken from the solution in this manner will be some function of the relative vapor pressure of the solution. Greater deviations from the true equilibrium condition may thus exist in the least concentrated solutions.

The last two explanations both account for the general nature of curve B. Further experimentation will be necessary, however, to prove that either or both are effective. The data nevertheless show that measurements like those of Barkas (2) in concentrations that do not appreciably depress the relative vapor pressure do not measure the true surface-bound

water, and that only in solutions that depress the relative vapor pressure more than 25 per cent can approximations of the surface-bound water be made. Innumerable other investigations in which the "bound water" has been obtained by determining the non-solvent water or water that does not freeze at an arbitrary temperature are subject to the same error of neglecting the activity of the water. This would be especially true in the case of water-insoluble capillary-active materials in which capillary effects would be most appreciable.

The adsorption of water from solution by the wood, if extended to solutions in equilibrium with zero per cent relative vapor pressure, should follow approximately the dashed part of curve B, figure 2. At relative vapor pressures below 20 to 30 per cent the solution should begin to remove surface-bound water from the wood. Curve B falls below curve A in the low relative vapor pressure range, presumably because the surface-bound water shares its bonds between the wood and the adjacent solute molecules. If half of the bonds were shared in this manner, the surface-bound water would be twice the non-solvent water. In such a case the data would be in excellent agreement with the predictions.

SUMMARY

Adsorption measurements from aqueous solutions of sucrose, glycerol, and sodium chloride by wood all give selective adsorption of water. In none of these solutions is wood swollen beyond the water-swollen dimensions. Preliminary measurements of adsorption from solutions causing swelling beyond the water-swollen dimensions indicate that positive adsorption of solute is taking place. The selective adsorption of water from aqueous solutions is a function of the activity of the water in the solution. A constant value of 3 per cent is approached in equilibrium with reductions in the relative vapor pressure exceeding 25 per cent, which presumably is the adsorption value free from residual capillary condensation and non-equilibrium effects. This value is about half of the predicted surface-bound water. The difference between the values is explained on the basis of the surface-bound water acting as a partial solvent, sharing its bonds between the wood and adjacent solute molecules.

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THE RATE OF REACTION OF AMALGAMS WITH ACIDS. II

SODIUM AMALGAMS¹

WILBUR G. DUNNING AND MARTIN KILPATRICK

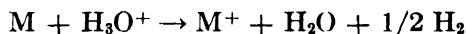
*Laboratory of Physical Chemistry, University of Pennsylvania,
Philadelphia, Pennsylvania*

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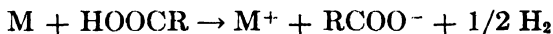
In a previous paper (3) it was shown that the rate of reaction of lithium amalgams with acids in the general sense followed two different kinetic laws. For the strong acids and the weak acids, with the exception of *o*-chlorophenol, it was found that the rate of appearance of the alkali metal ion in the solution was given by the relationship

$$\frac{dx}{dt} = kSC_A \quad (1)$$

where S is the surface and x is the number of ions of alkali metal formed at time t by way of the reaction



or

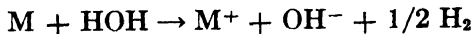


The rate appeared to be independent of the concentration of the alkali metal in the amalgam, and k varied with the acid used.

For the reaction with water or with buffer solutions of primary and secondary phosphate the rate equation is

$$-\frac{dC_M}{dt} = k'SC_A \cdot \sqrt{C_M} \quad (2)$$

where C_M is the concentration of the alkali metal in the amalgam and the reaction presumably is



and



¹ This paper is abstracted in part from the dissertation of Wilbur G. Dunning presented to the Faculty of the Graduate School of the University of Pennsylvania in partial fulfillment of the requirements for the degree of Doctor of Philosophy, December, 1935.

Equation 2 is in agreement with the results of Brönsted and Kane (2). These authors worked with dilute (0.024 molar) sodium amalgam and practically constant acid concentration. Moriguchi and Mitsukuri (11), working with amalgams ranging from 0.6 to 1.2 molar, found the velocity of reaction in hydrochloric acid solutions to be independent of the amalgam concentration and approximately proportional to the acid concentration. Klein (8) worked with high and practically constant concentrations of sodium in the amalgam and found that the results could be expressed by an equation equivalent to the first two terms in equation 1 of the paper of Fletcher and Kilpatrick (3). However, the first term could not be evaluated exactly, as the results in alkaline solution were not reproducible.

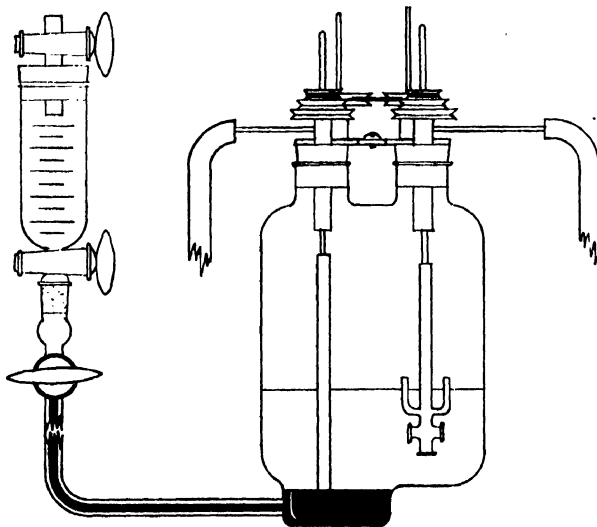


FIG. 1. Reaction vessel for amalgams

This lack of reproducibility for the water reaction has been observed by others. Baker and Parker (1, 12) observed that the rate of reaction of sodium with water varied with the purity of the water. They ascribed this to the presence of traces of hydrogen peroxide.

The purpose of the present work is to provide a further experimental test of equations 1 and 2, and to attempt to elucidate the results obtained by other workers. To do this a series of experiments has been carried out under different experimental conditions with various acids.

EXPERIMENTAL METHOD

The preparation of amalgams and the general procedure have been given by Fletcher and Kilpatrick (3). Three different reaction vessels were used and will be referred to as vessels D, F, and H. Figure 1 shows apparatus H equipped with stirrers for both solutions. In most experiments the

stirrer for the amalgam was removed. The area of the interface was 12.3 cm.² and 300 cc. of aqueous solution was used in most experiments. Apparatus D was similar in size and shape to apparatus H, the essential

TABLE 1
Experiments with hydrochloric acid at 25°C.

INITIAL CONCENTRATION OF ACID	INITIAL CONCENTRA- TION OF AMALGAM	REVOLUTIONS PER MINUTE OF STIRRERS		<i>k</i>	REMARKS
		Aqueous layer	Amalgam layer		

Apparatus D—area, 3.8 cm.²

moles per liter	moles per liter			cm. min. ⁻¹	
0.0150	0.31	2450	0	2.91	
0.0250	0.35	2450	0	1.79	
0.0250	0.35	2450	0	2.41	
0.0150	0.31	1650	0	1.48	
0.0300	0.31	1650	0	1.56	
0.0090	0.31	1650	0	1.74	
0.0100	0.24	1650	0	1.21	
0.1610	0.35	1650	0	1.31	
0.3220	0.35	1650	0	1.13	
0.0250	0.35	1650	0	1.78	
0.0250	0.35	1650	0	1.60	
0.0250	0.35	1650	0	1.39	
0.0300	0.56	1650	0	1.36	
0.0200	0.56	1650	0	1.35	
0.0260	0.56	1650	0	1.39	
0.0500	0.56	1650	0	1.39	
0.0300	0.66	1650	0	1.32	
0.0204	0.35	1660	0	1.65	
0.0204	0.35	1660	0	1.60	
0.0300	0.56	1650	0	1.41	<i>T</i> = 20°C.
0.0500	0.56	1650	0	1.54	<i>T</i> = 20°C.
0.0300	0.56	1650	0	1.61	<i>T</i> = 30°C.
0.0500	0.56	1650	0	1.76	<i>T</i> = 30°C.
0.0250	0.35	1150	0	1.17	
0.0250	0.35	1150	0	1.18	
0.0100	0.24	980	0	1.28	
0.0150	0.31	975	0	1.15	
0.0150	0.31	520	0	0.59	
0.073	0.57	500	0	0.67	
0.029	0.57	500	0	0.66	
0.010	0.57	500	0	0.60	
0.0250	0.35	500	0	0.69	
0.0250	0.35	500	0	0.65	
0.0540	0.27	500	0	0.65	
0.0540	0.27	500	0	0.87	In 0.95 <i>M</i> NaCl
0.0540	0.27	500	0	0.89	In 0.95 <i>M</i> NaCl
0.0540	0.27	500	0	1.03	In 0.95 <i>M</i> NaClO ₄

TABLE 1—*Concluded*

INITIAL CONCENTRATION OF ACID	INITIAL CONCENTRA- TION OF AMALGAM	REVOLUTIONS PER MINUTE OF STIRRERS		<i>k</i>	REMARKS
		Aqueous layer	Amalgam layer		
Apparatus D—area, 3.26 cm. ²					
moles per liter	moles per liter			cm. min. ⁻¹	
0.0412	0.56	2000	100	1.92	
0.0927	0.56	1950	0	1.62	
0.0927	0.56	1940	97	1.98	
0.0309	0.56	1900	95	2.00	
0.0618	0.56	1900	95	1.84	
0.0206	0.56	1900	95	2.14	
0.0399	0.90	800	75	1.88	
0.0250	0.90	850	60	2.10	In 1 <i>M</i> NaCl
Apparatus H—area, 12.3 cm. ²					
0.0299	0.33	1600	80	1.12	Volume = 200 cc. In 0.1 <i>M</i> NaCl
0.0199	0.33	1600	80	1.42	
0.00997	0.33	1600	80	1.33	
0.0299	0.33	1600	160	1.18	
0.0199	0.33	1500	75	1.28	
0.0299	0.33	1500	75	1.37	
0.0399	0.33	1500	75	1.44	
0.0100	0.24	1000	0	1.02	
0.0100	0.24	980	0	0.81	

difference being the cross section of the amalgam well, which was 3.26 in the early experiments and 3.8 in the later experiments. Apparatus F has already been described by Fletcher and Kilpatrick (3). The cross section of the well was 9.63 cm.² The general method of carrying out an experiment has already been given.

Table 1 summarizes the results with hydrochloric acid solutions. The velocity constants are calculated by the integrated form of equation 1.

Table 2 gives the results with perchloric acid. Inspection of the results with aqueous solutions of hydrochloric and perchloric acids indicates that the velocity constant is independent of the concentration of sodium in the amalgam, and from the agreement of the results with the two acids the rate of reaction is approximately proportional to the hydrogen-ion concentration with the possibility of an electrolyte effect. It is also evident that the rate of reaction is proportional to the surface of the amalgam. The effect of stirring of the amalgam is small and may be due to a change in the surface exposed to the aqueous solution. These results are essentially in agreement with the results with lithium amalgam.

Table 3 gives a comparison of the results with potassium and lithium amalgams.

From these results we can conclude that the velocity constants for all three amalgams are the same under the same experimental conditions. This suggests that the rate-controlling process is independent of the alkali metal in the amalgam, and we might conclude that this process is the trans-

TABLE 2
Experiments with perchloric acid at 25°C.

INITIAL CONCENTRATION OF ACID	INITIAL CONCENTRA- TION OF AMALGAM	REVOLUTIONS PER MINUTE OF STIRRERS		<i>k</i>	REMARKS
		Aqueous layer	Amalgam layer		
Apparatus D—area, 3.8 cm. ²					
moles per liter	moles per liter			cm. min. ⁻¹	
0.0400	0.56	1650	0	1.45	
0.0300	0.56	1650	0	1.31	
0.0200	0.56	1650	0	1.30	
0.0300	0.67	1650	0	1.29	
0.0050	0.60	500	0	0.83	
0.051	0.60	500	0	0.85	
0.010	0.60	500	0	0.82	
0.030	0.60	500	0	0.80	
0.030	0.60	500	0	0.88	
0.030	0.60	500	0	1.11	In 0.17 <i>M</i> NaClO ₄
0.030	0.60	500	0	0.91	In 0.34 <i>M</i> NaClO ₄
Apparatus D—area, 3.26 cm. ²					
0.0410	0.90	700	60	1.28	
0.0308	0.90	700	60	1.28	
0.0205	0.90	665	45	1.24	
0.0103	0.90	665	55	1.28	
Apparatus H—area, 12.3 cm. ²					
0.0103	0.90	1600	80	1.16	
0.0205	0.90	1600	80	1.11	
0.0410	0.90	1600	80	1.20	
0.0103	0.33	1600	80	1.20	
0.0205	0.33	1600	80	1.16	
0.0308	0.33	1600	80	1.14	
0.0308	0.90	1560	78	1.07	
0.0410	0.33	1560	78	1.13	

port of the acid to the amalgam surface. If this is the case, the effect of stirring, according to Roller (13), should be in agreement with the relation

$$\frac{k_{\text{obs.}}}{\omega^{0.8}} = \text{a constant}$$

where s is the rate of stirring. An examination of the results for apparatus D in table 1 gives an exponent which is approximately 0.7, but in the case of perchloric acid the exponent is considerably lower. Application of the equation

$$k_{\text{obs.}} = As^{0.8} (1 - e^{-k/As^{0.8}})$$

where $k_{\text{obs.}}$ is the observed velocity constant, k the chemical velocity constant, and A an empirical constant. If A is taken as 0.005 and the chemical velocity constant as 3.00, there is fair agreement between $k_{\text{obs.}}$ and the

TABLE 3
Comparison of velocity constants for alkali metal amalgams

AMALGAM	R.P.M.	<i>k</i>	REMARKS
Apparatus D—area, 3.8 cm. ²			
		<i>cm. min.⁻¹</i>	
Na.....	1650	1.43	Average of 14 experiments
K.....	1650	1.58	
Li.....	1650	1.43	
Li.....	500	0.78	Average of 7 experiments
Na.....	500	0.66	
Apparatus F—area, 9.63 cm. ²			
Na.....	975	1.06	Average of 7 experiments
K.....	975	1.01	
Li.....	975	1.07	
Apparatus H*—area, 12.3 cm. ²			
Na.....	1980	1.43	Average of 10 experiments
K.....	1980	1.42	
Li.....	1980	1.43	

* The experiments in apparatus H were carried out by Mr. K. Hoff, to whom due acknowledgement is made.

calculated velocity constants for the results in apparatus D. But if $k_{\text{obs.}}$ is the same for the three alkali metal amalgams in three different vessels, it would seem that the chemical k for lithium, sodium, and potassium would be the same. This seems hardly likely, so that one may conclude that an exponent of 0.67 is probably more nearly correct in the derivation of Roller. If that is the case, since $\frac{k_{\text{obs.}}}{s^{0.67}}$ is fairly constant, the conclusion

that the controlling process is the transport of the acid to the surface of the amalgam seems justified. If one considers a mechanism similar to that proposed by Sclar and Kilpatrick (14) for the dissolution of magne-

sium in alcoholic solutions of acids, the same general conclusion can be drawn.

EXPERIMENTS WITH WEAK ACIDS

In the experiments with weak acids buffer solutions were used at constant ionic strength for each series, so that the hydrogen-ion concentration

TABLE 4
Experiments with acetic acid at 25°C.

INITIAL CONCENTRATION OF ACID	INITIAL CONCENTRATION OF ACETATE	INITIAL CONCENTRATION OF CHLORIDE	INITIAL CONCENTRATION OF AMALGAM	REVOLUTIONS PER MINUTE OF STIRRERS		<i>k</i>	REMARKS
				Aqueous layer	Amalgam layer		
Apparatus D—area, 3.8 cm. ²							
moles per liter	moles per liter	moles per liter	moles per liter			cm. min. ⁻¹	
0.0210	0.0210 ⁶	0.170	0.56	1650	0	0.64	
0.0350	0.0350	0.150	0.56	1650	0	0.71	
0.0490	0.0490	0.130	0.56	1650	0	0.80	
0.0630	0.0630	0.110	0.56	1650	0	0.87	
0.0250	0.0250	0.175	0.56	1650	0	0.67	
0.0490	0.0490	0.151	0.56	1650	0	0.78	
0.0350	0.0350	0.150	0.56	1650	0	0.64	<i>T</i> = 20°C.
0.0250	0.0250	0.175	0.56	1650	0	0.64	<i>T</i> = 20°C.
0.0350	0.0350	0.150	0.56	1650	0	0.79	<i>T</i> = 30°C.
0.0250	0.0250	0.175	0.56	1650	0	0.71	<i>T</i> = 30°C.
0.0490	0.0490	0.130	0.34	1650	0	0.86	
0.0250	0.0250	0.175	0.31	1650	0	0.74	
0.0150	0.0150	0.185	0.31	1650	0	0.65	
0.20	0.20	0	0.60	500	0	0.41	
0.15	0.15	0.05	0.60	500	0	0.42	
0.05	0.05	0.15	0.60	500	0	0.54	
0.05	0.05	0.15	0.60	500	0	0.55	
0.05	0.05	0	0.60	500	0	0.51	
Apparatus H—area, 12.3 cm. ²							
0.054	0.0250	0.0250	0.33	1560	80	0.92	
0.027	0.0125	0.0375	0.33	1600	80	0.67	
0.036	0.0166	0.0334	0.33	1650	80	0.78	

was constant and negligible, as will be shown in a later section. The experiments with acetic acid buffers are shown in table 4.

Again the rate is independent of the amalgam concentration, and velocity constants are calculated in the same way as for the strong acids. The possibility that equation 2 might apply to these results will be considered after the presentation of the results for the water reaction.

Tables 5 and 6 present the results with other weak acids, and table 7 summarizes the results.

As in the case of lithium amalgams, the velocity constants are not very different. This can be interpreted to mean that we are dealing with a

TABLE 5
Experiments with weak acids at 25°C.
Apparatus D except as indicated

INITIAL CONCENTRA- TION OF ACID	INITIAL CONCENTRA- TION OF ANION	INITIAL CONCENTRA- TION OF CHLORIDE	INITIAL CONCENTRA- TION OF AMALGAM	REVOLUTIONS PER MINUTE OF STIRRERS		<i>k</i>
				Aqueous layer	Amalgam layer	
Mandelic acid						
<i>moles per liter</i>	<i>moles per liter</i>	<i>moles per liter</i>	<i>moles per liter</i>			<i>cm. min.⁻¹</i>
0.017	0.017	0.175	0.56	1650	0	0.54
0.024	0.024	0.165	0.56	1650	0	0.58
0.035	0.035	0.165	0.56	1650	0	0.59
Glycolic acid						
0.034	0.034	0.165	0.56	1650	0	0.61
0.024	0.024	0.175	0.56	1650	0	0.62
0.015	0.015	0.185	0.31	1650	0	0.61
0.040	0.040	0.160	0.31	1650	0	0.81
0.040	0.040	0.160	0.31	1650	0	0.71
0.100	0	0	0.60	500	0	0.44
0.100	0.100	0.100	0.60	500	0	0.40
Apparatus H—area, 12.3 cm. ²						
0.0370	0.0380	0.0125	0.33	1680	84	0.62
0.0122	0.0125	0.0375	0.33	1600	80	0.72
0.0244	0.0250	0.0250	0.33	1600	80	0.51
0.0489	0.0500	0	0.33	1600	80	0.67
Formic acid						
0.0260	0.0260	0.175	0.56	1650	0	0.78
0.0365	0.0365	0.165	0.56	1650	0	0.77
0.030	0.030	0.170	0.35	1650	0	0.70
0.015	0.015	0.185	0.35	1650	0	0.71
0.100	0.100	0.100	0.60	500	0	0.36
0.050	0.050	0.150	0.60	500	0	0.33

rate-controlling process involving a transport of the molecules of the carboxylic acid to the surface of the amalgam. If this were the case, however, the order of the velocity constants should be perchloric acid, hydrochloric acid, formic acid, acetic acid (7) and if hydrochloric acid is taken

as unity the ratios of the k 's to k for hydrochloric acid should be perchloric acid 1.1, formic acid 0.26, acetic acid 0.23. The actual ratios of the veloc-

TABLE 6
Experiments with weak acids at 25°C.

INITIAL CONCENTRA- TION OF ACID	INITIAL CONCENTRA- TION OF ANION	INITIAL CONCENTRA- TION OF CHLORIDE	INITIAL CONCENTRA- TION OF AMALGAM	REVOLUTIONS PER MINUTE OF STIRRERS		<i>k</i>
				Aqueous layer	Amalgam layer	
Phenylacetic acid						
<i>moles per liter</i>	<i>moles per liter</i>	<i>moles per liter</i>	<i>moles per liter</i>			<i>cm. min.⁻¹</i>
0.035	0.035	0.165	0.56	1650	0	0.58
0.025	0.025	0.175	0.56	1650	0	0.56
0.015	0.015	0.185	0.31	1650	0	0.52
0.030	0.030	0.170	0.31	1650	0	0.53
0.050	0.050	0.150	0.56	500	0	0.38
0.050	0.050	0.050	0.56	500	0	0.40
Propionic acid						
0.035	0.035	0.165	0.56	1650	0	0.82
0.010	0.010	0.190	0.56	1650	0	0.76
0.035	0.035	0.165	0.56	1650	0	0.66
0.022	0.022	0.178	0.56	1650	0	0.58
0.025	0.025	0.175	0.31	1650	0	0.63
0.015	0.015	0.185	0.31	1650	0	0.61

TABLE 7
Summary of experiments with weak acids

ACID	R.P.M.	AVERAGE k	AVERAGE DEVIATION
			<i>per cent</i>
Mandelic.....	1650	0.57	4
Formic.....	1650	0.74	5
	500	0.35	5
Glycolic.....	1650	0.65	10
	500	0.42	5
Phenylacetic.....	1650	0.55	4
	500	0.39	3
Acetic.....	1650	0.75	10
	500	0.49	11
Propionic.....	1650	0.68	12

ity constants at 1600 R.P.M. are perchloric acid 0.94, formic acid 0.52, acetic acid 0.52, and at 500 R.P.M. the ratios are perchloric acid 1.3, formic acid 0.54, acetic acid 0.75. From the data of Kilpatrick and Rushton (6)

with magnesium, the corresponding ratios are: perchloric acid 0.74, formic acid 0.33, acetic acid 0.21, while from the data of King and Cathcart (7) we have perchloric acid 0.97, formic acid 0.34, acetic acid 0.28. Whatever the relation between the velocity constant and the diffusion coefficient, these ratios should be the same for the dissolution of magnesium and of sodium amalgam. If we apply an equation of the type $k = \alpha D^x$, the value of x is approximately 0.45 for sodium amalgam. These computations indicate a lack of correlation between dissolution constants and diffusion coefficients. Further experiments with weaker acids indicated that the rate law was not that of equation 1, but that the kinetic law given by equation 2 was followed. In all previous experiments when the reaction was carried to completion the hydrogen evolved was found to correspond to the number of equivalents of sodium reacted. This was not true in the case of monochloroacetic acid or with cacodylic acid. The latter acid

TABLE 8
Experiments with phosphates

AQUEOUS SOLUTION	INITIAL CON- CENTRATION OF AMALGAM	R.P.M.	$10^3 (C_A k + k_w)$
0.030 M NaH_2PO_4	0.31	1650	2.0
0.030 M Na_2HPO_4			
0.20 M NaCl			
0.050 M NaH_2PO_4	0.31	1650	2.6
0.050 M Na_2HPO_4			
0.175 M NaH_2PO_4	0.56	1650	12.5
2.0 M NaH_2PO_4	0.56	500	62.0

is very easily reduced. With solutions of tertiary and secondary sodium phosphate the volume of hydrogen was always less than that calculated from the sodium reacted. In the case of the primary phosphate and mixtures of primary and secondary phosphates, the gas evolved corresponded to the sodium reacted. Table 8 gives these results, the acid concentration being constant. The velocity constant in column 4 is the sum of the water constant and the acid constant multiplied by the acid concentration.

In all cases the velocity constants have been calculated from the integrated form of equation 2 and confirm the results of Fletcher and Kilpatrick (3) with *o*-chlorophenol and those of Brönsted and Kane (2) with very weak acids.

THE WATER REACTION

With the exception of a few experiments which were followed by the gas evolution method, the experimental method for the water reaction was that used by Kilpatrick and Rushton (6) and by Fletcher and Kilpatrick (3). In view of the fact that the purity of the water seemed to make a

marked difference, all experiments were carried out with conductivity water and in most cases the water used was from a special batch having a specific conductance of 5×10^{-7} mhos at 25°C. Air was not excluded from the solution except in the case of the experiments followed by gas

TABLE 9
The water reaction

INITIAL AMALGAM CONCENTRA- TION	H ₂ O ⁺ CONCENTRATION	R.P.M. (AQUEOUS LAYER)	$k_w \times 10^3$	REMARKS
<i>moles per liter</i>	<i>moles per liter</i>			
0.31	1×10^{-9}	2450	1.60	
0.31	1×10^{-9}	1650	0.86	
0.31	1×10^{-9}	1650	2.20	
0.56	1×10^{-6}	1650	0.65	
0.35	1×10^{-6}	1650	1.00	
0.31	1×10^{-9}	1000	1.50	
0.05	1×10^{-6}	1000	0.70	
0.05	1×10^{-6}	800	0.68	
0.05	4×10^{-10}	500	0.26	
0.26	1×10^{-9}	500	0.16	
0.04	1×10^{-9}	500	0.45	
0.05	1×10^{-7}	500	0.40	
0.06	1×10^{-6}	500	0.55	
0.06	1×10^{-6}	500	0.30	
0.06	1×10^{-6}	500	0.32	Apparatus H—area, 12.3 cm. ²
0.01	1×10^{-6}	500	1.10	
0.01	1×10^{-6}	500	1.00	
0.01	1×10^{-6}	500	0.71	
0.04	1×10^{-4}	500	0.36	
0.01	1×10^{-4}	500	0.89	
0.60	Range 10^{-7} to 10^{-12}	500	0.18	By gas evolution
0.60		500	0.18	
0.25		500	0.12	
0.56		500	1.00	
0.26	1×10^{-9}	500	0.18	In 1 M KCl
0.26	1×10^{-9}	500	0.29	In 1 M LiCl
0.26	1×10^{-9}	500	0.17	In 1 M NaCl
0.26	1×10^{-6}	500	0.59	In 0.003 M CaCl ₂
0.26	1×10^{-6}	500	0.34	In 1.14 M CaCl ₂
0.33	1×10^{-9}	500	0.40	In 0.33 M SrCl ₂

evolution. The indicators used were bromophenol blue, methyl red, bromothymol blue, phenolphthalein, and thymol blue. The velocity constants were calculated from the integrated form of equation 2. C_{H_2O} , being a constant, is included in k . The results are presented in table 9.

All experiments are at 25°C., but it should be stated that there is very little effect of temperature.

A plot of the logarithm of the velocity constant against the logarithm of the stirring speed gives a line of slope of approximately 0.7. The velocity constant seems to be independent of the hydrogen-ion concentration within the reproducibility of the experiments. Since the average value of the velocity constant is smaller for the experiments carried out by the gas evolution method, the possibility of a reaction with oxygen was tested in a special series of experiments. In addition the effect of hydrogen peroxide was studied.

The results in table 10 are in qualitative agreement with those for lithium amalgams and indicate that there is a reaction with oxygen as

TABLE 10

Effect of oxygen and hydrogen peroxide

Initial concentration of amalgam, 0.78; R.P.M. = 1650; temperature = 25.0°C.

INITIAL CONCENTRATION OF H_2O_2	HYDROGEN-ION CONCENTRATION	10%	$\frac{10^3 (k - k_w)}{C_{H_2O_2}}$
<i>moles per liter</i>	<i>moles per liter</i>		
0	10^{-7} to 10^{-12}	0.53	By gas evolution
0	1×10^{-9}	0.67	Open to air
0	1×10^{-9}	1.06	Oxygen bubbled through the solution
0.036	1×10^{-9}	2.15	42
0.11	1×10^{-9}	3.15	23
0.11	1×10^{-5}	3.66	27
0.18	1×10^{-9}	6.05	30

well as with hydrogen peroxide (9). The reduction of oxygen would result in the formation of hydrogen peroxide (4) in acid solution.

Our experimental test of equation 2 was carried out at constant acid concentration. To test the possibility that equation 2 might be applied to the acetic acid buffer we have

$$-\frac{dC_M}{dt} = (k_w + k_A C_A) S \sqrt{C_M}$$

so that upon plotting $\frac{1}{C_M} \left(\frac{dC_M}{dt} \right)$ versus C_A a straight line of slope $-k_A S$ and intercept $-k_w S$ should result if the law is obeyed. Computations with the data for acetic acid indicate this law is not obeyed.

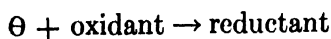
In calculating velocity constants for the strong and weak acids, with the exception of primary phosphate, equation 1 was used and the water

reaction was neglected in the calculation. It was realized that this neglect would lead to some discrepancies in the determination of the velocity constants. Computation by means of the equation

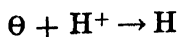
$$\frac{dx}{dt} = \frac{\bar{v}S}{1000} [k_w + k_{HB}C_{HB}] \sqrt{C_M} + S[k_{H_3O^+} \cdot C_{H_3O^+}] + S[k_A C_A]$$

(where \bar{v} is the volume of amalgam in cubic centimeters, HB represents an acid such as the primary phosphate, and A represents an acid such as phenylacetic) yields information concerning the portion of the alkali metal appearing in the solution by the various reactions. dx/dt is the number of gram-ions of sodium appearing per minute in the aqueous solution. These calculations indicate that the water reaction comes in to as much as 25 per cent in the lowest concentrations of acids following the law represented by equation 1. In the case of acids following the square-root law, the correction for the water reaction is carried out without difficulty, as shown elsewhere (2). For all the experiments with buffer solutions, computations show that the reaction with hydrogen ion is quite negligible. Equation 2 does not seem to fit any mechanism of the reaction which the present authors can offer (5, 10). One or two observations may be worth recording. In many cases an island of bubbles formed on the amalgam surface, and the larger the island the more rapid was the rate of reaction, as a rule. In cases of excess of strong acid over the number of moles of sodium in the amalgam, the reaction rate is practically constant, and just before the sodium has all reacted there is a sudden increase in rate. Here we have a reaction which is of the first order, but under the experimental conditions appears to be of zero order and completed in finite time.

From the results of this paper and the preceding one (3) it is evident that the rate of reaction of alkali metal amalgams with strong and fairly weak acids follows a first-order law, in agreement with the findings of earlier workers in the field. The velocity constants are independent of the concentration of the alkali metal in the amalgam. In solutions of weaker acids and low hydrogen-ion concentration the rate is proportional to the square root of the concentration of alkali metal in the amalgam, and the results may be interpreted as a chemically controlled rate of reaction between electrons and protons from the weak acids (2). In both cases the results can be interpreted from the point of view of the general theory of acids. In addition, one must also consider the process



analogous to



SUMMARY

1. The earlier and the more recent work on the dissolution of amalgams has been confirmed.

2. For strong acids and certain weak acids the rate of solution is independent of the concentration of the alkali metal in the amalgam if the experimental conditions are such that the water reaction is negligible. The rate is proportional to the concentration of strong acid above 1×10^{-4} moles per liter, is proportional to the surface, and is dependent upon the stirring. For the weaker acids the increase in rate above the water reaction is proportional to the acid concentration.

3. For the water reaction and the reaction with primary phosphate the rate of solution is proportional to the square root of the alkali metal concentration, independent of the hydrogen-ion concentration, and proportional to the acid concentration and to the surface.

4. In the presence of oxygen, hydrogen peroxide is formed and reacts with the sodium amalgam. This reaction explains in part the lack of reproducibility in the rate of reaction of amalgam with water.

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THE ADSORPTION OF THE VAPORS OF DIMETHYL, DIETHYL, AND DI-*n*-PROPYL ETHERS BY ACTIVATED CHARCOAL¹

J. N. PEARCE² AND P. E. PETERS³

Physical Chemistry Laboratory, The State University of Iowa, Iowa City, Iowa

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The theory of adsorption which is most in favor at the present time is the Langmuir hypothesis, or modifications of it, in which adsorption is recognized as due to physical or chemical forces acting through distances comparable with molecular dimensions. There are cases in which this theory is difficult to apply, owing perhaps to a lack of knowledge of all the factors involved, but no other hypothesis affords an explanation so general in scope and yet so definite in its applicability to individual adsorption phenomena. Attempts to correlate adsorption data with physical properties, such as surface tension, van der Waals constants, boiling points, molecular volumes, and dipole moments, have proved successful in isolated instances. Undoubtedly many of these are factors which influence adsorption, but adsorption processes are generally so complex that it is difficult to establish the dependence of such phenomena upon a single physical property.

In spite of the large amount of published data upon adsorption of vapors by charcoal there has been little possibility of comparison of results, owing to the differences in activities of the charcoals used, as well as in operating technique, and other variable factors. Some years ago a series of investigations was begun in this laboratory during which measurements of adsorption of a number of vapors have been made upon a specially prepared charcoal under standardized operating conditions, in an attempt to learn the influence of molecular structure of the vapor upon adsorption, and to test the various mathematical treatments of adsorption magnitudes. Papers published before the death of the senior author included investigations upon water, alcohols, ammonia, and amines (7), methane and its chlorine derivatives (6), monochloro derivatives of saturated aliphatic hydrocarbons (8), dichloro derivatives of saturated aliphatic hydrocarbons

¹ This paper is an abstract of a portion of a thesis submitted by P. E. Peters to the Graduate College of The State University of Iowa in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

² Deceased November 14, 1936.

³ Present address: North Shore Coke and Chemical Company, Waukegan, Illinois.

(4), and various ketones and esters (5). This paper briefly outlines the results obtained in a study of the adsorption of the vapors of dimethyl, diethyl, and di-*n*-propyl ethers.

From our present knowledge of adsorption processes it appears probable that these attractive forces act largely through certain atoms or groups in the vapor molecule. In the chlorinated hydrocarbons adsorption is influenced by the number and position of the chlorine atoms; with ketones and esters the C=O group appears to be the center of attraction. Analogously, we should expect adsorption forces to act through the —O— atom in the adsorption of ethers.

If adsorption does occur through the oxygen atom it is evident that the cross-section area of the adsorbed molecule in a plane perpendicular to the direction of the adsorption force increases by definite increments as we proceed through the ether series. The number of molecules of any ether adsorbed at or near saturation will be influenced by this cross-section area, or covering power, per molecule. Hence we should expect in this series, as in previous series, that at higher pressures the smallest molecules would be most highly adsorbed. At lower pressures, where this steric effect is practically inoperative, and where the adsorption forces appear somewhat similar to van der Waals forces, we should expect the most complex molecules to be most highly adsorbed.

The apparatus and technique employed are the same as previously described (6).

The dimethyl ether was obtained as a 40 per cent solution in sulfuric acid from the Eastman Kodak Company. This solution was introduced directly into an evacuated system, and the ether was released by the careful addition of water. The ether was dried before admission to the adsorption apparatus. The diethyl and di-*n*-propyl ethers were purified by washing and by distillation in a special fractionating column (2, 9) until products having substantially constant boiling points were obtained.

In tables 1, 2, and 3 x/m is the number of cubic centimeters (N.T.P.) of vapor adsorbed per gram of charcoal at the equilibrium pressure p (in millimeters).

At 183.14°C. diethyl ether appeared to decompose slowly in the presence of the charcoal. After admission of a sample of the vapor to the charcoal the pressure decreased to a minimum, and then gradually increased. At 235°C. this decomposition became so rapid as to render the results valueless. For the 183.14°C. isotherm the values of p recorded are the minimum values. At 181.66°C. di-*n*-propyl ether begins to show very slight evidence of decomposition. The di-*n*-propyl ether isotherms could not be continued to equilibrium pressures higher than the vapor pressure of the compound at 50°C. (the temperature of the air bath), owing to condensation in the adsorption apparatus.

TABLE 1
Adsorption of dimethyl ether vapor by charcoal

At 0.00°C.									
<i>p</i>	2.58	5.41	9.48	20.49	51.50	124.29	256.17	636.55	
<i>x/m</i>	29.71	43.98	58.88	78.72	97.11	110.23	117.70	128.26	
At 50.00°C.									
<i>p</i>	2.18	5.35	15.50	33.49	61.12	84.85	125.21	211.55	426.26
<i>x/m</i>	8.68	17.56	31.75	45.03	56.55	63.60	70.97	80.95	92.30
At 99.37°C.									
<i>p</i>	3.82	10.62	18.40	34.69	74.47	125.88	205.06	258.95	397.52
<i>x/m</i>	4.44	9.20	13.92	20.54	30.05	37.84	46.15	50.20	57.76
At 139.41°C.									
<i>p</i>	16.17	32.25	89.11	170.53	213.85	350.69			
<i>x/m</i>	5.53	9.12	17.77	25.50	28.70	35.95			
At 182.64°C.									
<i>p</i>	30.07	115.90	243.09	305.01	429.48				
<i>x/m</i>	3.99	10.70	17.39	20.25	24.39				

TABLE 2
Adsorption of diethyl ether vapor by charcoal

At 0.00°C.									
<i>p</i>	0.35	1.59	2.04	3.57	15.77	51.55	97.25	138.62	181.60
<i>x/m</i>	25.74	48.64	58.14	69.03	79.62	84.34	87.89	91.29	94.06
At 34.60°C.									
<i>p</i>	0.45	1.94	12.66	54.89	94.01	210.39	452.01	652.31	
<i>x/m</i>	32.36	55.14	68.08	74.89	76.64	79.79	84.06	87.84	
At 40.00°C.									
<i>p</i>	0.52	0.65	1.94	5.18	34.69	130.99	252.35	399.95	551.48
<i>x/m</i>	19.50	34.31	51.64	59.94	70.52	75.31	77.88	79.91	82.24
At 99.65°C.									
<i>p</i>	0.94	2.73	10.32	33.10	98.98	196.18	286.24	374.90	649.27
<i>x/m</i>	14.52	26.52	38.46	49.27	57.95	61.71	63.68	65.51	67.88
At 138.85°C.									
<i>p</i>	4.09	18.90	37.12	85.79	175.05	318.03	637.76		
<i>x/m</i>	15.94	28.68	35.12	43.02	49.00	53.22	56.27		
At 183.14°C.									
<i>p</i>	13.19	29.52	50.81	90.05	143.09	188.09	236.18	329.60	507.62
<i>x/m</i>	8.20	16.50	22.42	28.54	33.59	36.37	38.77	41.72	45.44

Equilibrium pressures for the ethers were attained in a relatively short time. At the higher pressures the time for the attainment of equilibrium was from five to six hours. The rate of adsorption decreased with an increase in the size of the adsorbed molecule.

We have attempted by graphic methods to fit our data to various mathematical equations, but we have found no formula which fits the data throughout the temperature and pressure ranges studied. Langmuir's equation expressing adsorption on amorphous adsorbents (1), such as charcoal, becomes so complex that it cannot be satisfactorily subjected to experimental verification without more knowledge of the nature of such

TABLE 3
Adsorption of di-n-propyl ether vapor by charcoal

At 0.00°C.

$p \dots$	0.25	0.30	3.22	8.83	16.25	16.29
$x/m \dots$	29.07	49.23	60.87	65.00	70.25	74.96

At 50.00°C.

$p \dots$	0.10	0.30	0.40	1.78	11.00	36.36	92.33	149.38	187.53
$x/m \dots$	6.60	19.21	38.62	52.17	56.89	60.35	62.77	65.39	69.97

At 99.66°C.

$p \dots$	0.10	0.50	4.36	22.98	34.63	51.71	147.71
$x/m \dots$	11.06	25.98	41.85	47.53	48.59	49.07	51.19

At 139.55°C.

$p \dots$	0.25	1.68	12.04	37.94	81.88	110.95	142.69
$x/m \dots$	13.27	26.06	37.64	42.23	44.62	45.56	46.27

At 181.66°C.

$p \dots$	1.24	5.20	17.23	37.99	50.52	73.45	133.04
$x/m \dots$	14.57	23.02	29.02	33.91	35.52	37.30	39.78

surfaces. As an alternative we have plotted our data according to Langmuir's simplest relation, $x/m = abp/(1 + bp)$, for adsorption on plane surfaces. A plot of $p/(x/m)$ against p should be a straight line if this relation is applicable.

The isotherms plotted according to this method are shown in figure 1. For all isotherms except those of dimethyl ether at the higher temperatures this relation expresses the experimental points fairly well. The failure to comply with the formula at temperatures near and above the critical temperature is in disagreement with the results of McBain and Britton (3), who found the Langmuir equation to hold for the adsorption of nitrous

oxide, ethylene, and nitrogen at temperatures well above the critical temperature and at pressures up to 60 atm. It should be noted that the data for ethers fit the equation satisfactorily over a wider pressure range than did those for ketones and esters (5).

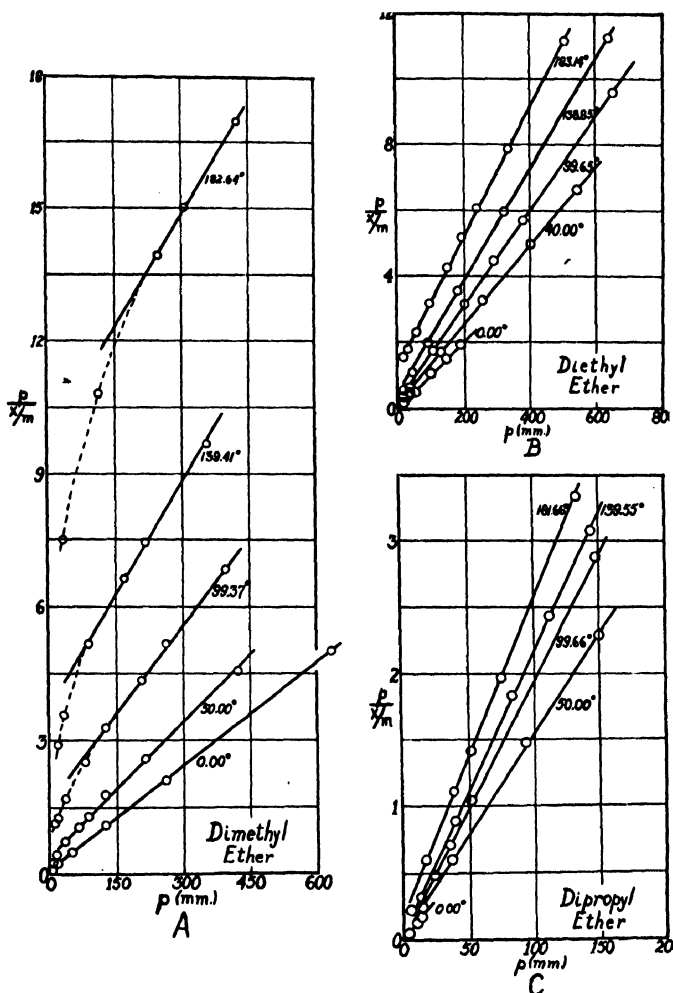


FIG. 1. The Langmuir adsorption isotherms for vapors of dimethyl, diethyl, and di-n-propyl ethers at various temperatures.

We have chosen the isotherms at the natural boiling points of the ethers for purposes of comparison of the adsorption magnitudes. At these temperatures the thermal energies of the molecules are equal, and the amounts of vapors adsorbed should be significant. Such a comparison is based upon the premise that the adsorption forces existing upon the surface of the adsorbent do not change throughout the temperature range investi-

gated, and that the amount of adsorption of any vapor depends upon the extent to which its thermal agitation prevents orientation of its molecules by the natural adsorption forces of the adsorbent.

The boiling point for dimethyl ether ($-24.9^{\circ}\text{C}.$) lies somewhat below the experimental temperature range. The isotherm for dimethyl ether at that temperature has been determined by extrapolation of the adsorption isobars (plot of $\log x/m$ against temperature).

The order of adsorption of the three ethers at their boiling points is shown in figure 2, in which $\log x/m$ is plotted against $\log p$. At low pressures, below about 0.5 mm., the order of increasing adsorption is dimethyl, diethyl, and di-*n*-propyl ethers; at higher pressures the order is reversed. These relations are similar to those previously found to exist in the series of ketone, ester, and chloride adsorptions. It is hardly necessary to point

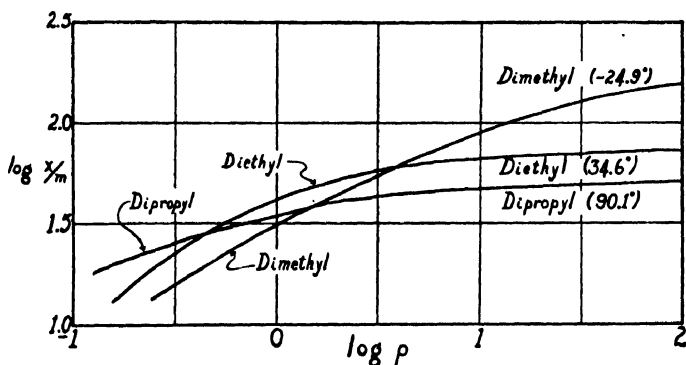


FIG. 2. Double-log isotherms of dimethyl, diethyl, and di-*n*-propyl ethers at their natural boiling points.

out the correlation at lower pressures between the order of increasing adsorption and the order of increasing van der Waals constants. At higher pressures this relation is reversed.

It should be noted that at higher pressures the order of adsorption may be correlated with van der Waals constant b more logically than with van der Waals constant a , as has been done in a previous publication (5). The constant a is a measure of the intermolecular attractive force between molecules of the vapor. The constant b is a measure of the volume of the vapor molecule. Hence if the adsorption magnitude is correlated with van der Waals a it should logically be a direct correlation. At low pressures this is true, since a for the ethers increases in the order dimethyl, diethyl, and di-*n*-propyl, which is the same as the order of adsorption. At higher pressures this has been cited previously (5) as an inverse correlation. When van der Waals b is considered, however, the correlation becomes logical at higher pressures, since it is in this range that steric effects

become operative. The constant b for the ethers increases in the order dimethyl, diethyl, and di-*n*-propyl. In other words, for the pressure range in which steric effects are present, the molecules having the largest volume (large values of b) are the least adsorbed. At pressures below this range we would expect no correlation between b and adsorption magnitudes. While this correlation appears applicable in all of the series studied, and may be useful for comparative purposes, it is not to be inferred that adsorption processes are dependent upon these factors alone.

From the slopes of the isosteres for the ethers the heats of adsorption have been calculated as follows: dimethyl ether, $-8,280$ cal.; diethyl ether, $-12,050$ cal.; and di-*n*-propyl ether, $-12,830$ cal. No experimental data are available for comparison with the above values. They are probably of the right order of magnitude, although in general it has been found that experimentally determined heats of adsorption are slightly higher than those calculated from the slopes of the isosteres.

SUMMARY

The adsorption of vapors of dimethyl, diethyl, and di-*n*-propyl ethers has been investigated at temperatures between 0° and 183°C . Except for the dimethyl ether isotherms at higher temperatures the Langmuir equation for adsorption on plane surfaces satisfactorily expresses the adsorption magnitudes through the pressure range studied. At low pressures the higher boiling ether is adsorbed more strongly; as the pressure is increased the order of adsorption is reversed. Heats of adsorption of the three ethers have been calculated from the slopes of the isosteres.

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STUDIES ON AGING OF FRESH PRECIPITATES. XVIII

THE MIXED-CRYSTAL FORMATION BETWEEN BARIUM SULFATE AND POTASSIUM PERMANGANATE

I. M. KOLTHOFF AND G. E. NOPONEN

*School of Chemistry, Institute of Technology, University of Minnesota,
Minneapolis, Minnesota*

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According to Grimm *et al.* (4, 5, 6, 10, 11) mixed-crystal formation between two chemical individuals may occur when the following conditions are satisfied: (1) the chemical building types of the two compounds must be the same; (2) the lattice types must be the same; (3) the lattice constants must be of the same order of magnitude. Similarity of chemical building types refers to pairs of compounds with the same number of cations and anions in which the corresponding ions are made up of the same number of atoms. The above conditions include not only the classical ones of mixed-crystal formation but also the formation of Grimm's "neuartige Mischkristalle." Examples of systems forming this new kind of mixed crystals are barium sulfate-potassium permanganate; barium sulfate-potassium fluoborate; calcium carbonate-sodium nitrate; lead sulfide-sodium bromide, etc. Grimm and his coworkers (4, 6) studied especially the new kind of mixed-crystal formation between barium sulfate and potassium permanganate. They coprecipitated potassium permanganate with barium sulfate and studied the properties of the red precipitate. Briefly, they found that the crystals were homogeneously colored; that the permanganate in the crystals was inert towards various reagents; that the rate of solution in concentrated sulfuric acid increased with the potassium permanganate content of the crystals; that the amount of potassium permanganate in the crystals was approximately proportional to the concentration of potassium permanganate in the precipitating solutions; that it was possible to obtain precipitates containing as much as 80 mole per cent of potassium permanganate; that the x-ray pictures made by the Debye method showed a regular displacement of lines (6, 11), such as would be produced if the potassium permanganate were dissolved in the barium sulfate lattice; finally, that equivalent amounts of potassium and permanganate are coprecipitated. The latter fact is strongly indicative of mixed-crystal formation; the results of the x-ray investigation of

Wagner (6, 11), however, give conclusive evidence of the formation of solid solutions of potassium permanganate in barium sulfate.¹

Various authors (1, 2, 3) have tried to invalidate Grimm's conclusions. Balarew (1), for example, criticizes Grimm's work and attributes the coprecipitation of potassium permanganate to an internal adsorption during the growth of barium sulfate. Balarew's claim that the coloring of barium sulfate by potassium permanganate is not completely homogeneous does not disprove mixed-crystal formation. Even in cases in which mixed crystals of the classical type are formed, a heterogeneous distribution often occurs (compare, e.g., Kolthoff and Noponen (8, 9) for the systems barium sulfate-lead sulfate and barium sulfate-barium chromate). It depends upon the manner of preparation of the mixed crystals whether they are homogeneous or not. Neither Wagner *et al.* nor his opponents have considered the conditions under which homogeneous mixed crystals are obtained, and therefore one cannot arrive at any exact statement of the rules determining the distribution of permanganate between solution and solid. Benrath and Schackmann (2), criticizing Grimm's conclusions, showed that fairly perfect barium sulfate, on being shaken for five weeks with potassium permanganate solutions, incorporated hardly any potassium permanganate. Such a result was to be expected, as hardly any recrystallization occurs upon shaking the fairly perfect barium sulfate. Interesting studies on the coprecipitation of permanganate with barium sulfate have been made by Karaoglanov (7), the results of which are in harmony with the concept of the formation of solid solutions.

It is peculiar that the authors criticizing Grimm's conclusions ignore the conclusive evidence of mixed-crystal formation obtained by him and Wagner from the x-ray diagrams.

In the present study the authors have made a preliminary study of the incorporation of potassium permanganate in recrystallizing barium sulfate with the ultimate purpose of learning the rules governing the distribution of potassium permanganate between the solid and liquid phases. In previous work by the authors (8, 9) it was shown that *homogeneous* mixed crystals of barium sulfate and lead sulfate and of the former with barium chromate could be obtained upon adding lead nitrate or sodium chromate, respectively, to a fresh suspension of barium sulfate and shaking for considerable periods of time until distribution equilibrium was attained. The fresh, imperfect barium sulfate is subject to repeated recrystallizations upon aging in the mother liquor, thus incorporating the mixed-crystal-

¹ After this paper was submitted for publication, P. R. Averell and G. H. Walden, Jr., (J. Am. Chem. Soc. **59**, 906 (1937)) reported conclusive evidence, based upon x-ray investigations, that hydronium permanganate (H_3OMnO_4) forms a solid solution in barium sulfate.

forming component in the recrystallizate, and eventually yielding homogeneous crystals. In the present study an attempt was made to reach distribution equilibrium from two sides: (1) by shaking freshly precipitated barium sulfate with solution containing potassium permanganate until the concentration of the latter in the solid became constant, (2) by shaking barium sulfate containing coprecipitated potassium permanganate with the supernatant liquid until the permanganate concentration in the solid became constant.

EXPERIMENTAL

A 0.5 molar solution of potassium permanganate was prepared and filtered through an asbestos filter after one day of standing. The general procedure was to precipitate barium sulfate quickly at room temperature from 0.3 *M* solutions of barium nitrate and sodium sulfate, using a slight excess of barium. Immediately after precipitation, various volumes of 0.5 *M* potassium permanganate were added and the suspensions shaken at room temperature (8, 9). After various periods of time the mixtures were centrifuged and the mother liquor was poured off. The precipitate was washed four or five times with 50-ml. portions of c.p. acetone which did not contain impurities reacting with permanganate. It was found that water could not be used for washing the precipitate, as permanganate was extracted continuously. With acetone, on the other hand, the fourth or fifth washing was always colorless. The washed precipitate was dried at 130°C. for twenty-four hours. Weighed amounts of the dried precipitate (from 0.3 to 0.8 g. depending upon the permanganate concentration) were treated with 10 ml. of concentrated sulfuric acid in a glass-stoppered iodine flask. After the crystals had completely dissolved, 40 ml. of water and 0.25 g. of potassium periodate were added, and the contents of the flask were heated for ten to fifteen minutes. The solution was then cooled and made up to a volume of 100 ml. The permanganate content of the solution was determined colorimetrically by comparing with suitable standards in a colorimeter, taking the average of ten readings.

The rate of entrance of permanganate into freshly precipitated barium sulfate

To 26 ml. of 0.3 *M* barium nitrate were added 25 ml. of 0.30 *M* sodium sulfate and 25 ml. of 0.5 *M* potassium permanganate. The mixtures were shaken for various periods of time and further treated as described above. The amounts of permanganate found in the precipitate after various periods of time are given in table 1. The occurrence of a maximum in the amount of permanganate in the precipitate after one day of shaking is comparable to that of lead in the precipitate upon shaking fresh barium sulfate with lead nitrate (8).

The rate of exit of coprecipitated potassium permanganate from barium sulfate

To a mixture of 26 ml. of 0.3 *M* barium nitrate and 25 ml. of 0.5 *M* potassium permanganate was added 25 ml. of 0.3 *M* sodium sulfate. The suspensions were shaken for various periods of time and further treated as described above. The amounts of permanganate found in the precipitate are reported in table 2. Apparently, the fresh precipitate obtained in the presence of permanganate contains much more permanganate than corresponds to equilibrium conditions. Grimm *et al.* (4, 5, 6) filtered their precipitates within half an hour after the preparation. Therefore their results do not correspond to a state of equilibrium, and no exact relation can be inferred from them regarding the distribution of the permanganate between the solid and liquid phases. Comparing the data in tables 1 and 2 shows that the same state of distribution of permanganate is approached

TABLE 1
Rate of entrance of permanganate into barium sulfate

Time of shaking.....	1 hour	22 hours	6 days	15 days	1 month
Milligrams of KMnO_4 per 1 g. of BaSO_4	9.6	11.3	8.1	8.3	8.3

TABLE 2
Rate of exit of coprecipitated permanganate

Time of shaking.....	10 minutes	1 hour	25 hours	7 days
Milligrams of KMnO_4 per 1 g. of BaSO_4	19.3	17.3	11.5	9.2

from both sides after sufficient periods of time of shaking, indicating that distribution equilibrium can be attained from both sides.

The amount of potassium permanganate in the mixed crystals as a function of the concentration of the former in solution

The experiments described in table 1 were duplicated, except that different volumes of 0.5 *M* potassium permanganate were added after the precipitation. The suspensions were shaken for one month, centrifuged, washed with acetone, etc. The results of table 3 tend to show that there is no linear proportionality between the amounts of permanganate in the solid and liquid phases. However, they are not quite conclusive, since it will be shown below that the amount of permanganate taken up by the solid decreases upon addition of sodium nitrate to the solution. In the above experiments the supernatant liquid contained sodium nitrate, the concentration of which decreased with increasing volumes of permanganate added. Moreover, it may be expected that the relative effect of sodium

nitrate upon the amount of permanganate incorporated in the solid will decrease with increasing concentration of potassium permanganate in the liquid. This effect of sodium nitrate may explain why the amount of incorporated permanganate increases more than linearly with the potassium permanganate concentration in the solution (table 3). The experiments will be repeated under conditions in which the effect of sodium nitrate is eliminated.

Effect of other salts upon the amount of potassium permanganate incorporated in barium sulfate

The experiments of table 1 were repeated, except that in addition weighed amounts of some electrolytes were added immediately after the precipitation to give mother liquors of various compositions. The sus-

TABLE 3
Relation between concentration of permanganate in solid and in solution

Milliliters of 0.5 M KMnO_4 added.....	50	10	5
Milligrams of KMnO_4 per 1 g. of BaSO_4	31.9	2.55	1.2

TABLE 4
Effect of salts upon distribution of permanganate

Composition of mother liquor*	0.2 M NaNO_3	1.6 M NaNO_3	1.3 M KNO_3 + 0.2 M NaNO_3	1.3 M NaCl + 0.2 M NaNO_3
Milligrams of KMnO_4 per 1 g. of BaSO_4	8.3	3.9	12.5	6.5

* The concentration of potassium permanganate in the mother liquor was 0.17 M.

pensions were shaken for one month in order to attain distribution equilibrium of the permanganate. It is seen (table 4) that the amount of permanganate incorporated in the barium sulfate decreases upon addition of sodium nitrate and sodium chloride, the effect of the former being greater than that of the latter. On the other hand, the distribution into the solid phase is favored by the addition of potassium nitrate.

DISCUSSION

It has been shown that the rate of establishment of the distribution equilibrium of potassium permanganate between barium sulfate and solution is small. The same equilibrium distribution is reached upon shaking when potassium permanganate is added to the fresh suspension of barium sulfate as when it is coprecipitated, indicating the formation of a solid solution. In the case of mixed-crystal formation in the classical sense ($\text{BaSO}_4 + \text{PbSO}_4$; $\text{BaSO}_4 + \text{BaCrO}_4$) we have shown (8, 9) that large

concentrations of electrolytes in solution, the ions of which do not participate in the exchange with ions in the lattice, do not affect the distribution of the isomorphous ion between the solid and the solution, if the added electrolyte does not change the ratio of the activities of the two isomorphous ions in the solution. Thus, it was found that the distribution of lead ion between barium sulfate and solution was not affected by 1 molar sodium nitrate and the distribution of chromate was not affected by 2 molar ammonium acetate. The system barium sulfate-potassium permanganate differs from the above classical systems in as much as indifferent electrolytes, such as sodium nitrate and sodium chloride, decrease the amount of permanganate taken up by the solid under equilibrium conditions. In interpreting these results it should be considered that Walden and Cohen (12) found that barium nitrate can be incorporated into barium sulfate in the form of a solid solution. Although barium nitrate, and possibly also other salts, which are not expected to form solid solutions in barium sulfate according to the classical rules or those of Grimm, do not affect the distribution of an isomorphous ion, they apparently do affect the distribution in the case of the formation of the new kind of mixed crystals of the type described by Grimm. The decreasing effect of sodium nitrate upon the distribution of the potassium permanganate in the barium sulfate may be responsible for the fact that no linear relation has been found between the concentration of potassium permanganate in solution and in the solid under equilibrium conditions. If such a linear relation exists within a certain range of mole per cent of potassium permanganate in the solid, it might be represented by the following expression:

$$(c_{K^+} \cdot c_{MnO_4^-})_{\text{solution}} = K(c_{KMnO_4})_{\text{solid}}$$

in which concentrations are written instead of activities. According to this expression addition of potassium salt to the solution should favor the distribution of permanganate in the solid phase. Actually, addition of potassium nitrate to the solution was shown to have the expected effect (table 4). Apparently the increasing effect of the potassium ions is greater than the decreasing effect of nitrate ions upon the distribution of the potassium permanganate in the solid phase.

From this preliminary study it may be inferred that the factors determining the distribution are much more involved in the case of the formation of the "new kind of mixed crystals" than in the case of the distribution of an isomorphous ion between solid and solution. The investigations are being continued.

SUMMARY

1. Upon shaking freshly precipitated barium sulfate with a potassium permanganate solution, distribution equilibrium is reached after fifteen

days to one month. The same equilibrium is reached when the permanganate is coprecipitated with the barium sulfate and the suspension shaken for a period of about fifteen days. The amount of coprecipitated permanganate decreases considerably during the time of shaking.

2. Sodium nitrate, and to a lesser degree sodium chloride, in the solution decreases the equilibrium concentration of potassium permanganate in the solid phase.

3. The presence of sodium nitrate in the mother liquor may account for the fact that the concentration of potassium permanganate in the barium sulfate under equilibrium conditions was found to increase more than linearly with the potassium permanganate concentration in the solution.

4. Potassium nitrate added to the liquid increases the distribution of potassium permanganate in the solid phase. This is accounted for by assuming that within certain limits the distribution of potassium permanganate is given by the expression

$$(c_{K^+} \cdot c_{MnO_4^-})_{\text{solution}} = K(c_{KMnO_4})_{\text{solid}}$$

5. The factors affecting the distribution are more involved in the case of the formation of the "new kind of mixed crystals" than in the case of the distribution of an isomorphous ion between solid and solution.

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THE SYSTEM ZINC OXIDE-TITANIUM DIOXIDE. ZINC ORTHOTITANATE AND SOLID SOLUTIONS WITH TITANIUM DIOXIDE

SANDFORD S. COLE AND WALTER K. NELSON

*Research Laboratories, Titanium Division, National Lead Company,
Sayreville, New Jersey*

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INTRODUCTION

A previous paper from this laboratory (1) reported data on the crystal structure, temperature of formation, etc., of the yellowish pigment lead titanate. The data showed that lead titanate exists only in the metatitanate modification, PbTiO_3 . Zinc titanate also is of interest as a white pigment. The size of the unit cell of zinc orthotitanate, Zn_2TiO_4 , has been reported in the literature at various values. Holgerrson and Herrlin (3) reported $a_0 = 8.44$ A.U. for the product of the reaction $2\text{ZnO} + \text{TiO}_2$ using sodium chloride as a fluxing agent. Passerini (6) obtained a value of $a_0 = 8.41$ A.U. when $2\text{ZnO} + \text{TiO}_2$ was calcined at 900°C . for short periods of time. Taylor (8) reported $a_0 = 8.46$ A.U. for mixtures of $\text{ZnO} + \text{TiO}_2$ and $2\text{ZnO} + \text{TiO}_2$ after twenty-four hours' calcination at 1050°C . and indicated that zinc orthotitanate, Zn_2TiO_4 , was the only compound formed. The several investigators reported that the calcined product had a spinel structure typical of other compounds of the A_2BX_4 composition.

The existence of zinc metatitanate, ZnTiO_3 , has been claimed by Levy (4), Piperaut and Helbronner (7); Mellor (5), and Goodlass Wall and Lead Industries (2), but no experimental data were offered in substantiation. Zinc metatitanate, if formed, would be expected to have a crystal lattice resembling one of the other titanates of the MTiO_3 type, e.g., ilmenite, perovskite, etc.

In view of the discrepancies noted above, mixtures of titanium dioxide and zinc oxide from the composition $2\text{ZnO} \cdot \text{TiO}_2$ (ZnO , 67 per cent; TiO_2 , 33 per cent) to $5\text{ZnO} \cdot 7\text{TiO}_2$ (ZnO , 41 per cent; TiO_2 , 59 per cent) have been investigated over a rather wide range of temperature and time of calcination. The size of the unit cell for the several mixtures and calcinations was obtained as a means of observing the initial reaction temperature and other changes occurring during calcination.

METHOD OF PREPARATION AND EXAMINATION

Titanium dioxide precipitated from ilmenite solution and washed free of impurities was used as the source of pure oxide (over 99.8 per cent titanium dioxide, calcined basis). The principal impurity (silicon dioxide) in the titanium dioxide did not interfere in the reaction with zinc oxide, which was of highest purity, being over 99.9 per cent zinc oxide. The various mixtures were thoroughly mixed by blending in water, then filtering and drying. The calcinations were carried out in electrically heated muffles with the temperature controlled to within $\pm 5^\circ\text{C}$.

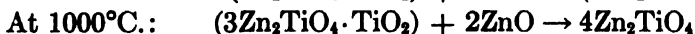
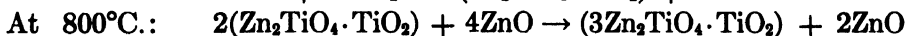
The x-ray diffraction patterns were obtained by mounting the samples on copper wire in a camera having a diameter of 57.30 mm. Copper radiations from a Ksanda gas type tube were used to obtain the pattern. The diffraction patterns were prepared in duplicate for each sample, so as to have a more correct value for the unit cell. The differences in the unit cell size never exceeded ± 0.005 A.U. in two different runs, and normally agreed within ± 0.002 A.U.

The determination of the titanium dioxide in the calcined samples was in accordance with standard methods: namely, dissolving the sample in concentrated sulfuric acid, reducing with zinc amalgam in a Jones reductor, and titrating the reduced solution with ferric ammonium sulfate using potassium thiocyanate as indicator. The titanium dioxide value is correct to within ± 0.1 per cent.

DISCUSSION

The initial reaction temperature between zinc oxide and titanium dioxide was found to be 430°C . Below this temperature, i.e., 400°C ., only ZnO and TiO_2 patterns resulted after heating for 144 hours. The reaction was 30 per cent completed at 450°C . after seventy-two hours. After 144 hours at 430°C ., the product was found to be a mixture of zinc oxide, titanium dioxide, and about 10 per cent of a compound having a spinel pattern with a unit cell size = 8.35 A.U. Heating a mixture of $2\text{ZnO} + \text{TiO}_2$ at higher temperatures yielded a product having different values for the unit cell and uncombined zinc oxide, as will be shown. The unit cell size increased and the uncombined zinc oxide decreased as the calcination temperature was raised.

The reactions occurring at 600°C ., 800°C ., and at 1000°C . are postulated to be as follows:



The range of stability of the solid solution, as will be shown, explains the discrepancies in the data reported by previous investigators. No evidence

was obtained which showed that zinc orthotitanate was the first product of the reaction, with excess titanium dioxide then reacting with it to yield a solid solution. The initial reaction product is, therefore, considered to be a solid solution of titanium dioxide in zinc orthotitanate of approximately the empiric composition ZnTiO_3 , i.e., $\text{Zn}_2\text{TiO}_4 \cdot \text{TiO}_2$ rather than ZnTiO_3 . Reaction of the excess zinc oxide with the solid solution is not rapid until the temperature is raised above 600°C . The reaction ($2\text{ZnO} + \text{TiO}_2$) is complete at 1000°C . (after twenty hours).

The solid solution series were heated at 700°C ., 800°C ., 900°C ., 950°C ., and 1000°C . The size of the unit cell and the composition at the temperature of stability for each mixture are given in table 1 and shown in figure 1. The value reported by Taylor for zinc orthotitanate, Zn_2TiO_4 , i.e., 8.46

TABLE 1

Size of unit cell of various compositions in the system TiO_2 - Zn_2TiO_4

NO.	COMPOSITION PER CENT TiO_2	MOLECULAR RATIO $\text{ZnO}:\text{TiO}_2$	SIZE OF UNIT CELL	TIME AND TEMPERATURE OF CALCINATION	
				hours	$^\circ\text{C}$.
A.....	32.96	2:1	8.460	20	1000
B.....	36.42	1.73:1	8.440	3	850
C.....	41.04	1.42:1	8.412	4	800
D.....	45.79	1.13:1	8.405†	4	900
E.....	47.64	1.09:1	8.380	4	800
F.....	50.15	1.04:1	8.372	16	750
G.....	52.8	0.97:1	8.371	4	750
H*.....	52.33	0.9:1	8.380	48	750
I.....	55.92	0.78:1	8.355†	16	750
J.....	59.00	0.7:1	8.344†	16	750

* Mixture of zinc orthotitanate and titanium dioxide before calcination.

† About 5 per cent uncombined titanium dioxide observed from diffraction patterns.

A.U., was checked. He reported that the mixture $\text{ZnO} + \text{TiO}_2$ after twenty-four hours at 1050°C . gave Zn_2TiO_4 and TiO_2 patterns; this also was found to be in agreement with our results. The limit of stability of the solid solution with respect to temperature increases as the composition approaches $2\text{ZnO} \cdot \text{TiO}_2$.

Diffraction patterns of ZnO , TiO_2 , Zn_2TiO_4 , and $\text{Zn}_2\text{TiO}_4 \cdot \text{TiO}_2$ are shown diagrammatically in figure 3. The data are calculated to d in Ångström units and the intensity is estimated for the lines.

The compositions marked F, G, H, I, and J dissociate above 800°C . into titanium dioxide and a solid solution poorer in titanium dioxide. The approximate field of stability of the solid solution has been indicated in figure 2, as based on results so far obtained. The upper limits of stability

were obtained by heating a given mixture for four hours at several temperatures and then obtaining the size of the unit cell for each heating

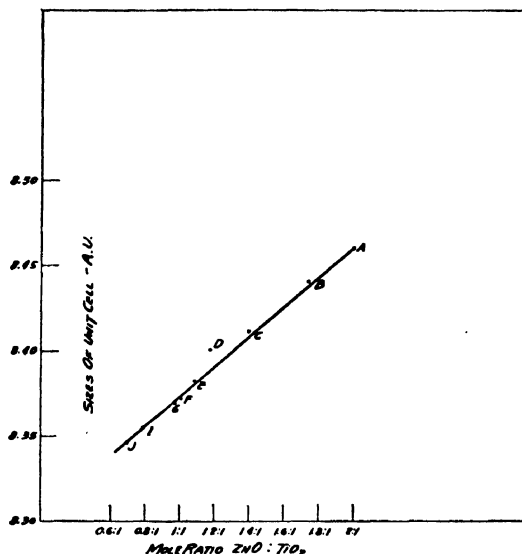


FIG. 1. Change of unit cell size in relation to composition

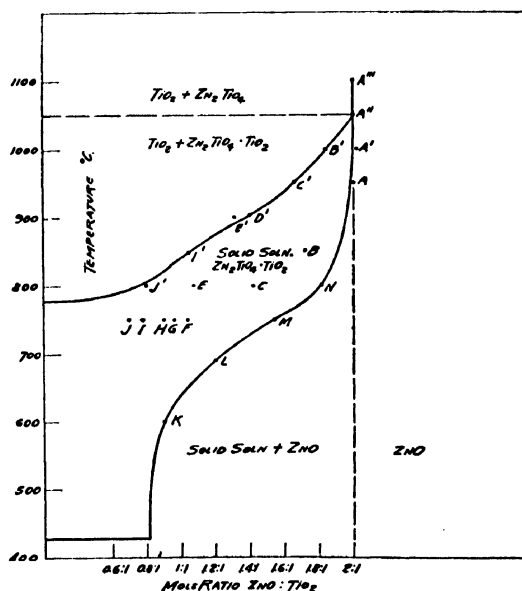


FIG. 2. Proximate limits of stability of solid solution $\text{Zn}_2\text{TiO}_4 \cdot \text{TiO}_2$

period. The dissociation of the solid solution could be determined from the change in the unit cell size. The composition of the product was

obtained from the curve in figure 1. For example, the composition of $1.73\text{ZnO} \cdot \text{TiO}_2$ (No. B) was heated at 1000°C . The unit cell size obtained was 8.45 A.U., which would compare with composition $1.86\text{ZnO} \cdot \text{TiO}_2$ according to the curve in figure 1. The proportion of zinc oxide in the composition has been increased by the splitting off of titanium dioxide from the solid solution which was stable at the lower temperature. Again, composition $1.04\text{ZnO} \cdot \text{TiO}_2$ (No. F) after heating at 950°C . had a unit cell of 8.43 A.U., which would be composition $1.65\text{ZnO} \cdot \text{TiO}_2$. All compositions except Nos. A and B, when heated at 950°C . gave 8.43 to 8.44 A.U. for the unit cell size. No comprehensive study of the stability of these solid solutions has been attempted, so that these temperatures are only

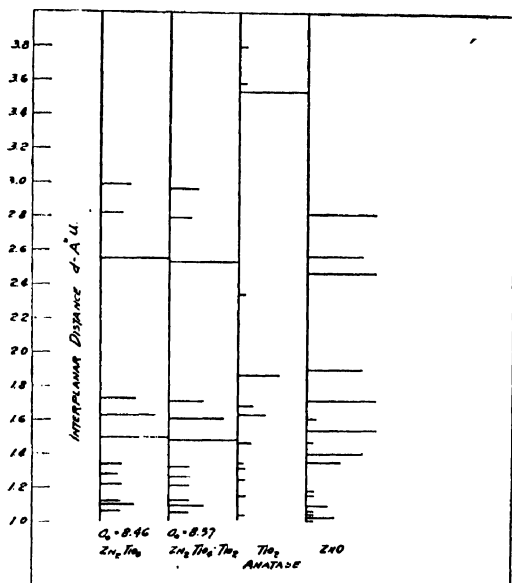


FIG. 3. Estimated intensity of principal diffraction lines

indicative of probable limits. The minimum temperature for dissociation of the solid solution is about 775°C . in the field rich in titanium dioxide.

Since the solid solution was found to be unstable, it was desirable to determine if the reaction was reversible. Consequently, the mixture (No. H) $\text{Zn}_2\text{TiO}_4 + \text{TiO}_2$ was heated for sixteen and forty-eight hours at 750°C . The Zn_2TiO_4 had been heated previously at 800°C . for sixteen hours and had a unit cell size of 8.45 A.U. The unit cell values became 8.42 A.U. and 8.38 A.U., respectively, showing that the titanium dioxide had been taken up slowly by the zinc orthotitanate. No TiO_2 lines were observed after forty-eight hours. The time required to bring about the change in the unit cell shows that the reaction is slow, but the final product is similar to the initial product of the reaction of $\text{ZnO} + \text{TiO}_2$ at 750°C .

The change in size of the unit cell of the reaction product of the mixture $2\text{ZnO} + \text{TiO}_2$, when heated for 24-hour periods at various temperatures, is given in table 2. The mixture was carefully blended so that the two reactants were in close contact. The data obtained check the results found in the calcination studies on mixtures having different $\text{ZnO}:\text{TiO}_2$ ratios. The reaction of $2\text{ZnO} + \text{TiO}_2$ is not completed until the temperature is above 900°C . for twenty-four hours. The reaction goes very slowly to completion, but is nearly complete above 800°C . with short periods of calcination (three to six hours) as observed from other data obtained but not reported.

TABLE 2

Size of unit cell of reaction product of $2\text{ZnO} + \text{TiO}_2$ at various temperatures

NO.	TIME	TEMPERATURE	SIZE OF UNIT CELL	REMARKS
	hours	$^\circ\text{C}$.	A. U.	
K.....	24	600	8.360	Approximately 30 per cent uncombined ZnO
L.....	24	680	8.382	Approximately 30 per cent uncombined ZnO
M.....	16	750	8.433	Approximately 15 per cent uncombined ZnO
N.....	16	800	8.450	Approximately 10 per cent uncombined ZnO
A.....	20	1000	8.459	
O.....	24	1100	8.460	

TABLE 3

Specific gravity of $\text{Zn}_2\text{TiO}_4 \cdot \text{TiO}_2$ and Zn_2TiO_4

	SOLID SOLUTION	ZINC ORTHOTITANATE
Composition.....	$(\text{Zn}_2\text{TiO}_4 \cdot \text{TiO}_2)$	Zn_2TiO_4
Observed gravity.....	4.76	5.12
Calculated gravity.....	4.79	5.28

In table 3 the observed and calculated specific gravity data for Zn_2TiO_4 and the solid solution $\text{Zn}_2\text{TiO}_4 \cdot \text{TiO}_2$ are given. The calculated value of $\text{Zn}_2\text{TiO}_4 \cdot \text{TiO}_2$ is based on the assumption that it is a mixture of 75 per cent Zn_2TiO_4 (sp. gr. 5.12) and 25 per cent TiO_2 (sp. gr. 3.85). The calculated gravity of Zn_2TiO_4 is obtained, by the regular calculation, from the size of the unit cell (8.46), assuming eight molecules to the unit cell. The observed and calculated values for $\text{Zn}_2\text{TiO}_4 \cdot \text{TiO}_2$ are in close agreement.

SUMMARY

1. The size of the unit cell of zinc orthotitanate has been checked and found to be 8.46 A.U.
2. The solid solution of titanium dioxide in zinc orthotitanate extends to the composition $\text{Zn}_2\text{TiO}_4 \cdot 1.5\text{TiO}_2$, with spinel structure persisting.

3. The solid solution is not stable at higher temperatures, dissociating into titanium dioxide and a solid solution poorer in titanium dioxide. The lowest dissociation temperature observed was 775°C.

4. An approximate field of stability has been indicated based on data so far obtained.

5. The initial temperature of reaction of titanium dioxide with zinc oxide is about 430°C.

6. The first product of the reaction is a solid solution with a unit cell size the same as the lower limit of the solid solution.

7. The specific gravity of zinc orthotitanate was calculated as 5.28 and observed as 5.12.

8. Titanium dioxide will react with zinc orthotitanate in the stable range of the solid solution to yield a product richer in titanium dioxide.

9. Zinc orthotitanate was the only compound found in the composition range studied.

The writers wish to acknowledge the advice and keen interest of J. L. Turner, Director of Research, National Lead Company—Titanium Division, in connection with this investigation, and to thank H. Espenschied, who determined the specific gravities.

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THE VISCOSITY OF OIL-WATER EMULSIONS¹

GEOFFREY BROUGHTON AND LOMBARD SQUIRES

*Department of Chemical Engineering, Massachusetts Institute of Technology,
Cambridge, Massachusetts*

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INTRODUCTION

Although the viscosity of concentrated emulsions is of considerable interest, it has received inadequate industrial and theoretical study. This may be traced to the complexity of the subject, many variables undoubtedly being of importance. Of these, the outstanding appear to be (1) volume concentration of the disperse phase, (2) rate of shear, or shearing force, (3) viscosity of the continuous phase, (4) viscosity of the disperse phase, (5) the stabilizer or emulsifying agent used, and (6) the particle size of the emulsion. Most investigators have considered the effects of the first and second variables, paying but little attention to the others involved. As will be seen, the nature of the disperse phase and the emulsifying agent cannot be neglected. For dilute suspensions, in which the small spherical particles can be considered to be rigid and substantially independent of each other, the viscosity is dependent only upon the volume concentration of the disperse phase. Einstein (3, 4) theoretically obtained the relation²

$$\mu = \mu_0(1 + 0.025V) \quad (1)$$

For dilute emulsions and suspensions this holds with a fair degree of accuracy (9). Besides mutual interference, deformation of the dispersed particles may occur, and Taylor (13) has shown theoretically that to correct for this Einstein's equation may be written

$$\mu = \mu_0 \left\{ 1 + 0.025V \left(\frac{\mu_i + 2/5\mu_0}{\mu_i + \mu_0} \right) \right\} \quad (2)$$

However, small drops behave substantially as solid bodies if their radius does not exceed a certain critical radius (1),

$$r = \sqrt{T/(\rho_i - \rho)g}$$

¹ This article is based on the work of the late Kenneth R. Moll (Thesis, Massachusetts Institute of Technology, 1933).

² For nomenclature see table 1.

For most ordinary stable emulsions the drop size lies below this critical radius, making any experimental test of Taylor's expression difficult.

Hatschek (5) derived an expression for concentrated emulsions

$$\mu = \mu_0 \left[\frac{1}{1 - \sqrt[3]{V}} \right] \quad (3)$$

which he was able to show held for an emulsion of paraffin oil in 0.75 per cent soap solution. With concentrated emulsions the rate of shear used in the viscosity determination becomes of importance, a point emphasized by Hatschek. As it is increased the apparent viscosity decreases, becom-

TABLE 1
Table of nomenclature

μ	= viscosity of emulsion
μ_0	= viscosity of solvent or continuous phase
μ_i	= viscosity of internal or disperse phase
μ'	= limiting viscosity of emulsion
μ'_r	= limiting relative viscosity of emulsion
μ'_y	= limiting relative viscosity of emulsion at which yield point appears
V	= volume concentration, per cent
T	= surface tension of disperse phase
ρ_i	= density of disperse phase
ρ	= density of continuous phase
h	= volume concentration correction factor (Sibree)
k	= calibration constant in R.P.M. centipoises per degree MacMichael
M	= deflection in degrees MacMichael
R	= R.P.M.
M_y	= yield point
a, b, c	= constants

ing almost constant at high shear. Most investigators have, therefore, attempted to correlate the viscosities at infinite shear. Sibree (10) attempted to verify the Hatschek equation, using paraffin-water emulsions to which 1 per cent of sodium oleate had been added as an emulsifier. The paraffin phase was weighted with bromoform, so that both phases possessed the same density.³ By insertion of a correction factor h , so that equation 3 becomes

$$\mu = \mu_0 \left[\frac{1}{1 - \sqrt[3]{hV}} \right] \quad (4)$$

substantial agreement with experiment was obtained. Sibree was of the opinion that this correction factor, about 1.3, was an expression of the

³ It will be noted that this prevents creaming and tends to make the drops deformable when the emulsion is under shear.

increased volume of the drops due to a hydrated film of the emulsifier around their surface. Although he stated that the value of the volume factor might be specific for a given emulsion, no attempt was made to use different emulsifying agents and disperse phases beyond comparing the viscosities of emulsions made with limpid and viscous paraffins. These were found to have substantially the same viscosity at equal volume concentrations (11). Air entrainment leads to greatly increased viscosity (7), which apparently accounts for the observation of Sibree that coarse emulsions had much lower viscosities than fine ones. When all air was carefully removed, both coarse and fine emulsions had substantially the same viscosity.

More recently Richardson has deduced on theoretical grounds the equation

$$\mu/\mu_0 = e^{cV} \quad (5)$$

obtaining good agreement with benzene in water emulsions stabilized with sodium oleate (8). Richardson again investigated but one dispersed phase and one emulsifying agent. Sibree's data, when plotted in the form $\log \mu/\mu_0$ against V , give straight lines which do not pass through the origin, although data of some other workers (8) conform to the Richardson formula. In view of the fact that most of the investigators to date have studied but one emulsion or one variable, it was felt that investigation of several emulsions at varying rates of shear using different stabilizing agents would be of value.

EXPERIMENTAL

The preparation of emulsions

Seven types of emulsions were prepared, using aqueous solutions of sodium oleate, saponin, and triethanolamine oleate (1, 2, and 3 per cent by weight, respectively) as continuous phases, and Nujol, benzene, and olive oil as the disperse phases. The materials used were of C.P. grade or its equivalent. To prevent creaming or separation of the disperse phase on standing, all the oils were weighted with α -bromonaphthalene to a specific gravity of 1.00, so that on standing for several days the most dilute emulsions showed no tendency to cream.

Emulsification was performed by adding appropriate quantities of the weighted oil to the solution of the emulsifier, and thoroughly stirring the mixture in a high-speed electric stirrer. Intermittent stirring was found to be most effective, and a definite schedule of 1 min. of stirring followed by 1 min. of rest was selected. For some of the emulsions, particularly those stabilized by triethanolamine oleate, little or no stirring was necessary, emulsification being almost spontaneous.

The emulsions prepared in this way were sometimes coarse and always contained an appreciable amount of air. For removal of this a vacuum homogenizer, such as recommended by Briggs (2), was found satisfactory. All emulsions were given four or more passes through the homogenizer and showed no change in viscosity on standing for several weeks.

Viscosity determinations

The MacMichael viscosimeter was used in this investigation. It consists of an inner disc, suspended by a torsion wire inside an outer cup, which can be rotated at any constant speed desired. In all the experiments the viscosimeter was allowed to run at the indicated speed until the deflection of the wire became constant, four or more points in all being taken on the R.P.M.-deflection curves. The temperature is maintained constant ($25^{\circ} \pm 1^{\circ}\text{C}.$) by means of the water bath surrounding the cup.

TABLE 2
Viscosity of liquid phases at 25°C.

PHASE	VISCOSITY
	<i>centipoises</i>
Benzene.....	0.82
Nujol.....	33.2
Olive oil.....	121.0
1 per cent sodium oleate solution.....	0.983
3 per cent sodium oleate solution.....	1.138
2 per cent saponin solution.....	1.001
3 per cent triethanolamine oleate solution.....	4.730

Three torsion wires were required to cover the range of viscosities encountered in this investigation. The viscosity was calculated from the R.P.M. and deflection by the relation

$$\mu = k \cdot \frac{M}{D} \quad (6)$$

the calibration constants, k , of the wires being obtained by measurements at $25^{\circ}\text{C}.$ against a 60 per cent sugar solution. The value of the viscosity of this solution was taken as 44 centipoises (6).

The viscosities of the phases, listed in table 2, were determined in an Ostwald viscosimeter, except that of the weighted olive oil, which was measured in the MacMichael viscosimeter.

RESULTS

When the viscosities of the various emulsions are calculated it is found, in agreement with the results of other investigators, that this quantity is

not a constant for any given emulsion, but varies with the rate of shear. All the emulsions behave as non-Newtonian liquids, e.g., figure 1 shows the variation for an emulsion containing 50 volume per cent of weighted Nujol in 3 per cent aqueous triethanolamine oleate solution. Thus the asymptote of the viscosity rate of shear curve (the limiting viscosity) or viscosity at infinite shear will be chosen as the quantity for consideration in the following discussion.

The experimental data for all the emulsions were plotted as R.P.M.-deflection curves, representative straight lines being drawn through the

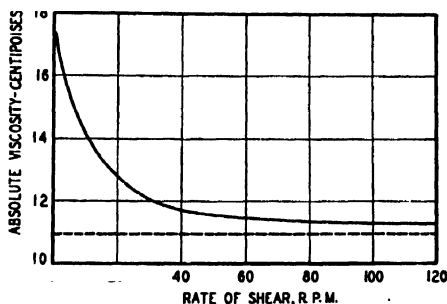


FIG. 1

FIG. 1. Effect of rate of shear on viscosity for emulsion 10

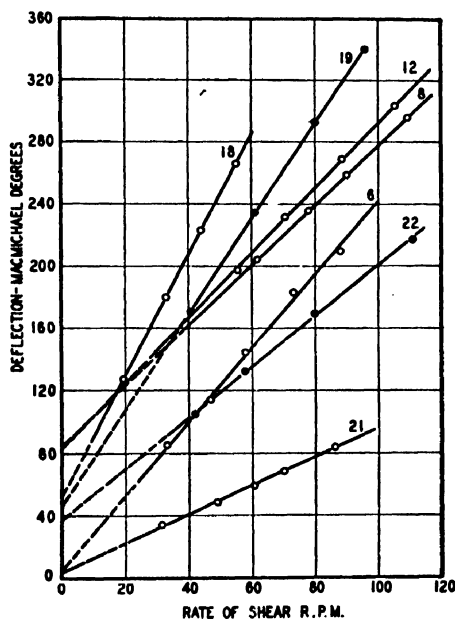


FIG. 2

FIG. 2. Torque-rate of shear diagram. Wire X; temperature = $26^{\circ} \pm 1^{\circ}\text{C}$.

See table 3 for key to figures

points. Typical curves are shown in figure 2. It is obvious that the slopes of the straight-line portions are inversely proportional to the limiting viscosities. These slopes were determined, and the limiting viscosities are listed in column 4 of table 3. At very high rates of shear the points begin to deviate from this straight line, becoming concave to the deflection axis.⁴

If the R.P.M.-deflection curves are extrapolated to low rates of shear it is found, in most cases, that they do not pass through the origin but

⁴ Taylor (12) has shown that this condition occurs when the flow ceases to be laminar and becomes vertical or turbulent.

intersect the torque axis at a definite positive value. This point of intersection has been termed the yield point, and represents the theoretical distorting force necessary to initiate flow. While there is doubt as to

TABLE 3
Summary of calculated data

EMULSION	VOLUME PER CENT (OIL)	YIELD POINT	LIMITING VISCOSITY	RELATIVE LIMITING VISCOSITY
			<i>centipoises</i>	
Nujol-sodium oleate				
4	50	1.94	8.94	9.09
2	60	5.0	14.75	15.0
8	70	84.0	29.9	30.4
3	75	178.5	37.5	38.15
Nujol-saponin				
5	50	0.54	10.97	10.97
6	60	5.0	36.3	36.3
9	70	440	78.5	78.5
7	75	838	143.8	143.8
Nujol-triethanolamine oleate				
10	50	2.9	10.97	2.31
11	60	8.0	18.85	3.98
12	70	83.0	32.45	6.87
27	80	1320	92.3	19.5
Benzene-triethanolamine oleate				
14	50		8.02	1.70
15	60		12.07	2.55
16	70		32.10	6.78
26	75	27.5	66.5	14.05
Benzene-sodium oleate				
20	50	0.97	9.05	7.95
21	60	4.0	14.13	12.42
22	70	36.0	25.2	22.1
Olive oil-triethanolamine oleate				
17	50	24	22.95	4.85
18	60	50	60.30	12.72
Olive oil-sodium oleate				
24	50	0.32	8.90	7.82
24	55	8.0		20.9

whether this extrapolated value is a definite physical entity, nevertheless it is obvious that, knowing the value of the yield point and the limiting viscosity, the flow characteristics of the emulsion can be calculated over the range where the R.P.M.-deflection relation is linear. In such cases,

over wide ranges the two quantities,—the extrapolated yield point and the limiting viscosity,—define the viscous behavior of the emulsion. In column 3 of table 3 are listed the yield points determined by extrapolating the R.P.M.—deflection curves and expressed in terms of the equivalent deflection that would have been produced had one common wire been used for all the emulsions.

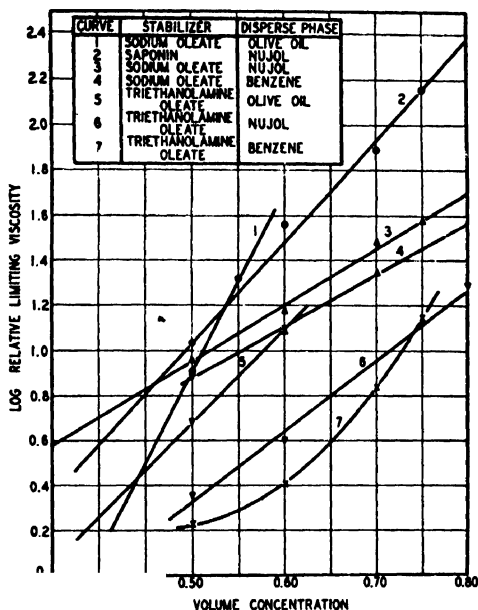


FIG. 3

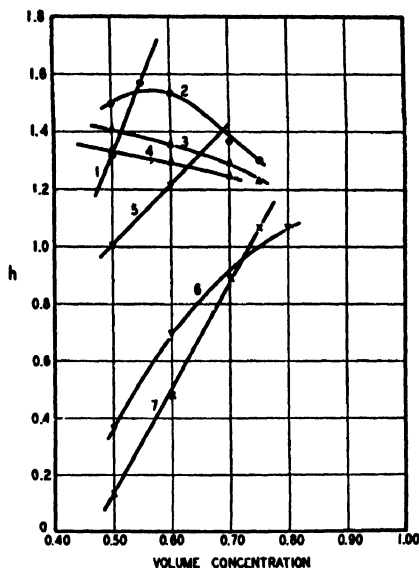


FIG. 4

FIG. 3. Relative viscosity versus volume concentration

FIG. 4. Sibree correction factor h versus volume concentration of disperse phase.
See figure 3 for key to figures

DISCUSSION OF RESULTS

The effect of volumetric concentration

Inspection of the values of the limiting viscosity given in column 4 of table 3 shows that this quantity varies with the concentration over a wide range of values. It is therefore more convenient to plot not the limiting viscosity itself but its logarithm. Furthermore, to place the various emulsions on a comparative basis it is preferable to plot the logarithm of the limiting relative viscosity, defined as the ratio of the limiting viscosity to the viscosity of the continuous phase.

Examination of figure 3 shows that the logarithm of the limiting relative viscosity is linear in the volumetric concentration for the majority of the emulsions studied and hence may be represented by the equation

$$\text{Log } \mu'_r = a + bV \quad (7)$$

This relationship is somewhat analogous to that of Richardson (equation 5). Since the present data when extrapolated to $V = 0$ do not show relative limiting viscosity of unity, equation 5 does not hold.

Curve 7 of figure 3, showing the viscosity for the benzene-triethanol-amine oleate emulsion, cannot be represented by a straight line and is an exception to the generalization given above. This may be related to the fact that this emulsion shows no yield point up to 70 per cent concentration.

The Hatschek equation, as modified by Sibree, may be expressed as

$$h = \left(\frac{\mu_r' - 1}{\mu_r'^3} \right)^3 / V \quad (8)$$

Figure 4 shows the value of h calculated according to this equation plotted against the volumetric concentration for the data of table 3. If the data followed equation 2, h would lie uniformly on the line $h = 1$. If it followed equation 3 a series of straight lines parallel to the concentration axis, but having a different value for each emulsion, would be obtained. It is evident that no such behavior was found; in some cases h decreased with increasing concentration and for the Nujol-saponin emulsion even exhibited a maximum. If h were a measure of the percentage increase in volume of the disperse phase due to the layer of hydrated stabilizer around each particle, as suggested by Sibree, it would necessarily always be greater than unity. However, curves 6 and 7 of figure 4 show values of h far below unity at the lower volumetric concentrations, excluding such an interpretation. Hence, it can be seen that the Hatschek equation or its modification is not of general applicability.

It is interesting to note that h is most nearly constant for emulsions of hydrocarbons stabilized by sodium oleate (curves 3 and 4), which are the type Sibree prepared. While the slopes of the lines in figure 4 are smallest for these types, even in them considerable variation in h occurs. In fact, Sibree's own data show a variation in h from 1.45 at a volume concentration of 0.5 to 1.28 at 0.75 volume concentration for the viscous paraffin emulsion. Furthermore, for his data h always decreased with increasing volumetric concentration, although in many cases the decrease was not so marked as in the example quoted above. Considering figure 4, this change in h is significant and corroborates the present data, although Sibree concluded from his experiments that h was constant.

The results as shown in figures 3 and 4 indicate that the volumetric concentration of the emulsion is not the only important variable influencing the limiting relative viscosity.

Variation of the yield point

Inspection of column 3 of table 3 shows that the yield point as defined above varies even more widely with concentration than does the limiting viscosity. It is well known that relatively dilute emulsions behave like true liquids, showing no yield point and hence no variation in viscosity with rate of shear. Above a fairly definite concentration, however, the viscosity becomes a function of the rate of shear and a yield point develops.⁵ All the emulsions studied were in a concentration range well above this limit, with the exception of the benzene-triethanolamine oleate emulsion (curve 7, figure 3). This emulsion showed no yield point up to a volume concentration of 0.70. In table 4 are listed the estimated concentrations at which a yield point appeared, obtained by linear extrapolation of the

TABLE 4
Volume concentration and viscosity at initial yield point

EMULSION	VOLUME CONCENTRATION AT WHICH YIELD POINT APPEARS	CORRESPONDING LIMITING RELATIVE VISCOSITY, μ'_l
		<i>centipoises</i>
Nujol-sodium oleate.....	0.437	5.5
Nujol-saponin.....	0.489	11.0
Nujol-triethanolamine oleate.....	0.440	1.65
Benzene-triethanolamine oleate.....	0.718	8.7
Benzene-sodium oleate.....	0.465	6.0
Olive oil-triethanolamine oleate.....	0.407	1.8
Olive oil-sodium oleate.....	0.445	6.0

yield point-concentration curve. The third column of table 4 also shows the limiting relative viscosity of the emulsion at this concentration.

If the logarithm of the yield point is plotted against the logarithm of the difference between the limiting relative viscosities at the corresponding concentration and at the concentration at which the yield point appears, the curves shown in figure 5 are obtained. While it is to be admitted that these calculations are based on somewhat questionable extrapolations, the plot indicates an interesting though approximate correlation, the points seriously off the curve lying at low volume concentrations where accurate estimation of the yield point is difficult. It will be observed that the logarithm of the yield point is linear with the logarithm of the viscosity difference and that the curves have the same slope. This would indicate that the yield point is a function of the type of stabilizer and limiting vis-

⁵ In certain emulsions the behavior may be more complex, the fluid showing anomalous viscosity before development of a yield point.

cosity of the resulting emulsion. Hence it would appear that if, at one volumetric concentration, the yield point and limiting viscosity were known together with μ'_y , the viscous behavior over a wide range of concentrations could be quantitatively predicted by the relations shown in figures 3 and 5.

No generalizations can be made as to the influence of the viscosity of the disperse phase on the resulting viscosity of the emulsion. Curves 5, 6, and 7 of figure 3 show that the viscosities of emulsions at the same volumetric concentration and for the same stabilizer are in the order of the viscosities of the disperse phases. However, this relation is reversed for the benzene and Nujol emulsions at 75 volume per cent. Again, compar-

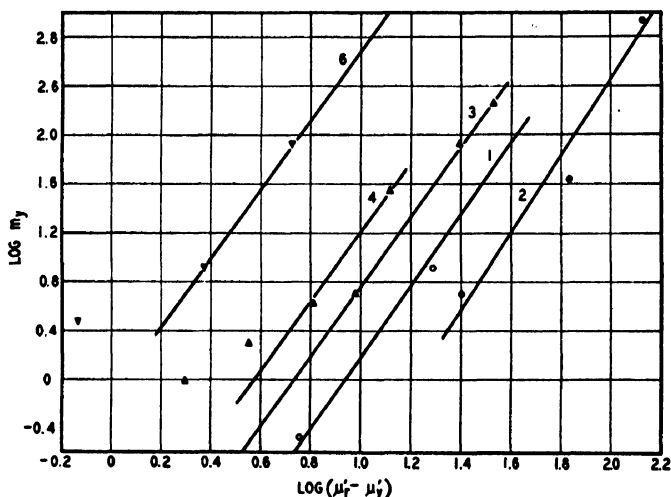


FIG. 5. Logarithm of the yield point plotted against the logarithm of the difference between the limiting relative viscosities at the corresponding concentration and at the concentration at which the yield point appears. See figure 3 for key to figures.

ing curves 1 and 4 for olive oil and benzene stabilized by sodium oleate, the viscosities of the more concentrated emulsions are in the order of the viscosities of the disperse phases, but at 50 volume per cent the viscosities of the two emulsions are identical.

The effect of stabilizers

The effect of the type of stabilizer on the viscosity of a given phase pair may be observed by comparison of the appropriate curves of figure 3 (curves 2, 3, and 6 for Nujol-water, curves 4 and 7 for benzene-water, and curves 1 and 5 for olive oil-water). It will be seen that for a given phase pair the limiting relative viscosity at a definite concentration varies widely with the type of stabilizer employed. For curves 2, 3, and 6 the variation in viscosity at the same concentration is in the order of increasing ease of

emulsification, the most efficient stabilizer producing the emulsion of lowest viscosity. Thus triethanolamine oleate emulsified Nujol practically spontaneously, but the saponin emulsion was quite difficult to prepare. The same order is shown in curves 4 and 7 for the benzene emulsions and in curves 1 and 5 for the olive oil emulsions.

Without doubt, the effect of the stabilizer is exceedingly important. Thus, the relative viscosity at 70 volume per cent of Nujol-water emulsions stabilized with saponin and triethanolamine oleate varied thirteenfold. It is true that difference in particle size may, in part, account for this variation but, in view of the work of Sibree already referred to, this appears unlikely. The influence of the stabilizer may, however, well account for some of the confusing results obtained in the past by different investigators.

CONCLUSIONS

1. The viscosity of a concentrated emulsion is a function of the rate of shear, approaching an asymptote as the rate of shear is increased. Over wide ranges the relation between shearing stress and rate of shear is linear. For a given emulsion, i.e., a given phase pair and stabilizer concentration (based on the dispersing medium), the limiting viscosity at infinite rate of shear increases with the volume concentration of the disperse phase. The quantitative relation between the concentration and the limiting viscosity is best represented by a modified form of the Richardson equation. The Hatschek equation, as modified by Sibree, does not apply.

2. Other than volumetric concentration, the type of stabilizer employed seems to be the variable of most significance in determining the magnitude of the viscosity of any phase pair. Stabilizers producing the best emulsification give emulsions of the lowest limiting relative viscosity.

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THE SYSTEM GALLIUM-INDIUM

SIDNEY J. FRENCH, DONALD J. SAUNDERS,¹ AND GEORGE W. INGLE

Department of Chemistry, Colgate University, Hamilton, New York

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During the past two years the writers have studied a series of some forty alloys of gallium and indium covering the entire range of composition from pure gallium to pure indium. Search of the literature reveals no previous study of such alloys, this lack of study being due, no doubt, to the previous scarcity of the two metals.

In 1936 a progress report² was presented covering the determination of the eutectic in the system gallium-indium. The present paper includes that work (which was not published) and completes the study of this alloy system.

EXPERIMENTAL

Because of the relatively high cost of the metals involved it was essential to work with small amounts and to develop a technique suitable to such work. In the customary methods for studying alloy systems amounts up to 15 or 20 g. are used and time-temperature curves are plotted. The eutectic alloy may be squeezed out and analyzed.

In place of the usual time-temperature curve, the writers used *temperature-temperature* curves in which the temperature of the alloy was plotted against the temperature of its bath. This method is, of course, possible only where the alloys concerned have low melting points. Time was kept as nearly constant as possible in all determinations, the rate of temperature change being approximately one degree per minute.

An iron-constantan thermocouple prepared of fine wire and coated with high-grade white shellac was used for determining the temperature of the alloy. During the work on the gallium side of the curve the alloy was used as the variable cold junction, the hot junction being placed in a constant-temperature bath of boiling water. The hot junction assembly was specially prepared and consisted of a Kjeldahl flask, to one side of the

¹ Present address: Department of Chemistry, University of Wisconsin, Madison, Wisconsin.

² "The Eutectic in the Gallium-Indium System," presented before the Division of Industrial and Engineering Chemistry at the Ninety-second Meeting of the American Chemical Society, Pittsburgh, September, 1936.

neck of which an arm carrying a reflux condenser was sealed in. The thermocouple was inserted through a lower opening, so that the junction was immersed in water in an inner glass tube, the tube having an opening in the side to admit the thermocouple and to maintain a constant water level (see figure 1). A thermometer for checking the temperature was suspended in the tube. However, during the work on the indium side of the curve, with temperatures above $100^{\circ}\text{C}.$, it was found more convenient to reverse the thermocouple junctions. The constant cold junction was a specially constructed ice bath, consisting of a Dewar flask containing a test tube of cottonseed oil; this in turn contained the thermocouple junction which was admitted to the tube by an adequate length of glass tubing (see figure 2). The alloy itself became the variable hot

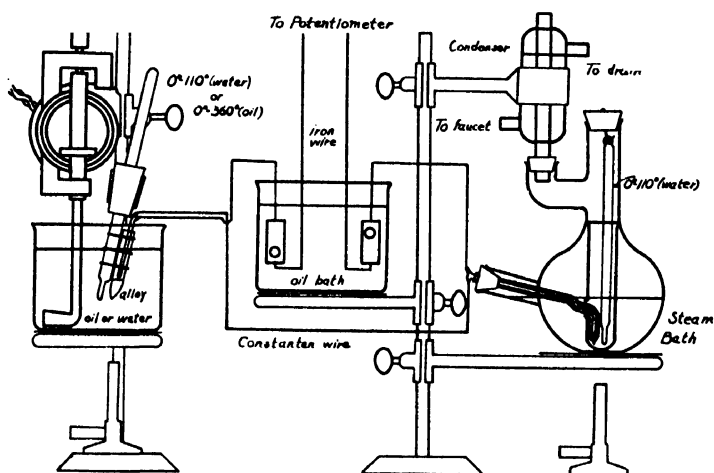


FIG. 1. Apparatus showing constant hot junction

junction. It was placed in a thin-walled closed glass tube of 5 mm. bore with a pointed, rather than a snub-nosed, end to relieve the expansive effect of the freezing alloy. The tube was attached to the bulb of the standardized thermometer by rubber bands, and was heated in a cottonseed oil bath to the required temperatures. In each case a sensitive d'Arsonval wall galvanometer, suitably damped, a potentiometer, and a standard cell with the usual accessories completed the assembly.

The thermocouple was calibrated by placing the cold junction first in ice water, while the hot junction was in the boiling bath assembly. The cold junction was next attached to the bulb of the standardized thermometer, and both were immersed in an 800-cc. water bath, the temperature of which was slowly raised to $100^{\circ}\text{C}.$, while the E.M.F. was plotted against the recorded temperature of the bath. The values obtained agreed with the

commonly assigned values for this thermocouple. The thermocouple was next checked by putting it in the thin-walled glass tube containing a little mercury, the tube being attached to the bulb of the thermometer. Again the whole was immersed in the water bath, which was stirred by a motor-driven stirrer. The bath was slowly heated and cooled several times while simultaneous readings of the thermometer and the E.M.F. were taken. The E.M.F. readings were translated to equivalent temperatures and plotted against temperatures of the bath recorded by the thermometer. This data indicated that there was no time lag in the temperature changes of the alloy, for temperatures of bath and alloy agreed at all points and gave practically a straight-line graph.

The method used, in which temperature of alloy is plotted against that of a neutral body, gives a differential curve known as the Roberts-Austen

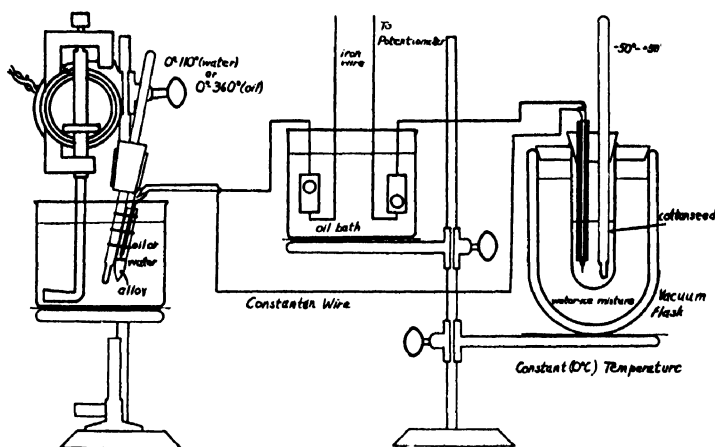


FIG. 2. Apparatus showing constant cold junction

differential curve. The chief advantage of the differential curve over the time-temperature curve lies in the fact that over a considerable range of temperatures the differential curve gives a *straight* line. If the same temperature interval is used in plotting temperature both of alloy and of bath, the line has a slope of 45° , the only deviations from a straight line coming at points which indicate a phase change in the alloy.

The gallium used was obtained from Eimer and Amend, the indium from the Indium Corporation of America. Since the cost of gallium prohibited the preparation of a large number of *separate* alloys, the method used was to add successive small increments of either gallium or indium to the original small amount of the other pure metal. Starting with 0.94 g. of gallium and adding successive increments of 0.01 g. of indium gave a series of gallium-rich alloys on the gallium side of the curve. Although

gallium is difficult to handle and cut, since it melts at a low temperature and is quite brittle, an analogous procedure was used to give a corresponding series of indium-rich alloys on the indium side of the curve.

In use, the thermometer with tube attached was immersed in the 800-cc. water or oil bath which was stirred with a motor-driven stirrer. Since gallium-rich alloys showed a strong tendency to supercool, it was necessary when working with such alloys to bring the temperature of the bath down to 0°C. to insure solidification of the alloy. The bath was then warmed up regularly with a small flame, and the corresponding E.M.F. for every degree increase in temperature was recorded. Water was placed above the

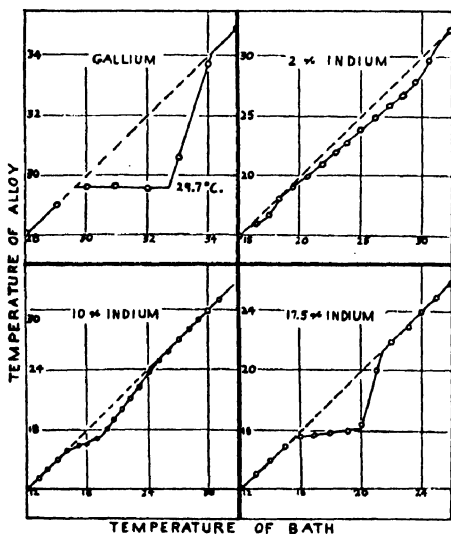


FIG. 3

FIG. 3. Melting curves of gallium and of alloys of indium with gallium

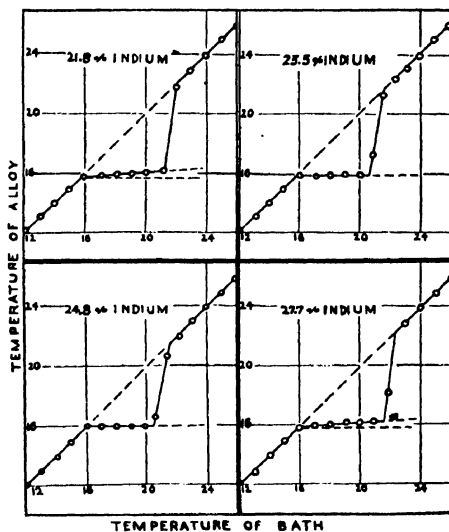


FIG. 4

FIG. 4. Melting curves of alloys of gallium and indium approximating the eutectic composition

alloy in the tube to prevent the metal from clinging to the glass and climbing.

By this method the melting point of pure gallium was determined and was found to be 29.7°C. The melting curve is shown in figure 3 (upper left). Successive increments of 0.01 g. of indium were then added. In each case the alloy was warmed up to about 50°C. to insure solution of the indium, though the indium appeared to dissolve in molten gallium at temperatures as low as 30°C. without difficulty. The alloys were kept molten for some time while the tube was vibrated to insure complete mixing. A minimum of three determinations was made on each alloy. The procedure with the indium-rich alloys on the indium side of the curve was similar, with similar precautions taken to insure complete solution.

Since any error in weighing the increments of either metal would be cumulative, producing errors in the calculated percentage of each succeeding alloy, great care was exercised in weighing the samples of indium and gallium. Later, several check alloys were prepared on either side of the eutectic range to determine, if possible, whether mistakes had been made in previous weighings. Since the curves for these alloys agreed with those of the former alloys, it was concluded that no errors had been made in the successive weighings.

Throughout an entire series of operations it was not necessary to remove the thermocouple from the alloy; thus it was assured that none of the alloy was lost during the work.

Because of the marked tendency of gallium-rich alloys to supercool, it was impossible to use cooling curves on the gallium side of the eutectic range. Instead, melting curves were used for these alloys. For the indium-rich alloys, however, it was possible to use both melting and cooling curves and thus determine the liquidus points with a high degree of accuracy. Readings of the thermometer were taken at 1° intervals, together with the corresponding thermocouple readings. With a little practise, it was found that one observer could take both readings. There appeared to be little or no oxidation of the alloys in the course of the work. This is undoubtedly due to the fact that only low temperatures are necessary.

DETERMINATION OF THE EUTECTIC COMPOSITION

Since it was impossible to squeeze out sufficient eutectic alloy from the small amounts used to conduct an analysis, and since, even were this possible, there are no satisfactory methods developed for the quantitative separation and estimation of these metals, and finally, since the use of such a scheme would alter the composition of the residual alloy and prevent the use of the method involved, i.e., that of adding successive increments to a previous alloy, it was necessary to determine the eutectic composition as nearly as possible by the temperature studies.

Alloys closely approximating the eutectic composition give curves indistinguishable from the curve of a true eutectic alloy. Hence it is not possible to determine the exact eutectic composition by means of temperature curves. However, it is possible by such means to "bracket" the eutectic composition, by noting those alloys lying on either side of the eutectic composition in which the curve first deviates slightly from that of the alloys within the eutectic range. Of the alloys studied the only ones which gave perfectly horizontal lines during phase change were those containing 23.6 and 24.8 per cent indium (see figure 4). Those nearest on either side containing respectively 22 and 27.7 per cent indium were definitely outside the eutectic zone (see figure 4). This narrows the eutectic range down to that lying between about 23 and 26 per cent indium.

A check on those values is obtained when the entire system has been worked out and the liquidus curves plotted on both sides of the eutectic range. Using smooth curves through the liquidus points in the temperature-composition diagram, it is found that these curves meet the proper temperature ordinate of 16°C . at a composition ordinate representing 24 per cent indium (see figure 7). Points on the gallium side of this curve may, however, be slightly in error, owing to the fact that they had to be taken from melting-curve data rather than cooling-curve data. However, they yield a smooth curve and are probably accurate to within a degree.

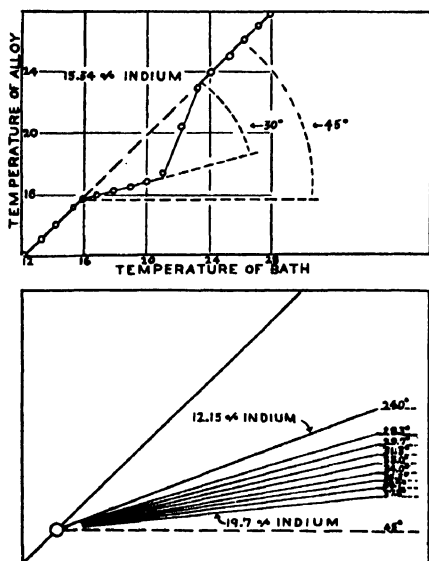


FIG. 5

FIG. 5. The upper part of the diagram illustrates the method used to determine the minimum eutectic range composition; the lower part gives the slopes of the melting curves of pro-eutectic alloys.

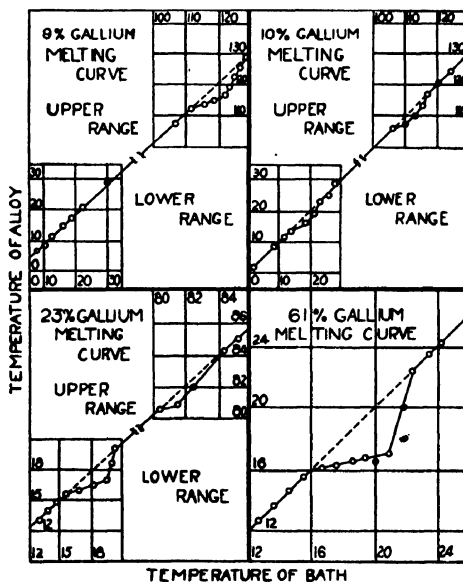


FIG. 6

FIG. 6. Melting curves of indium-rich alloys

(The points used are those at which there is a definite deviation toward the perpendicular in the melting curve.)

There appeared to be another method for checking the eutectic composition which became evident when the differential curves were plotted for a number of the gallium-rich alloys. It was found that such alloys containing 12 per cent or more (up to 20 per cent) indium gave curves which during phase change were perfectly straight lines based on four or more points (see figure 5, upper portion). The slope of this line appeared to bear a simple relationship to the percentage of indium present, approaching the horizontal as the indium increment was increased. Knowing the

percentage of indium present and the slope of the line, it was a simple matter to calculate the percentage of indium necessary to give a line with

TABLE 1
Calculation of eutectic range

PER CENT INDIUM IN ALLOY	ANGULAR SLOPE OF MELTING CURVE	MEAN SLOPE	CALCULATED VALUE OF EUTECTIC RANGE PER CENT INDIUM
	<i>degrees</i>	<i>degrees</i>	
12.15	23	24	22.70
	24		23.40
	25		22.00
14.55	29	28.2	22.70
	28		23.40
	28		23.40
15.34	31	29.7	22.30
	30		23.00
	29		24.00
16.07	33	31.3	22.00
			24.10
			23.30
16.80	34	33	22.20
	33		23.00
	32		23.70
17.54	35	34	22.50
	32		25.00
	35		22.50
18.26	34	35.3	24.20
	36		22.80
	36		22.80
19.00	36	36.7	23.80
	37		22.80
	37		22.80
19.66	37.5	37.8	23.60
	38.0		22.50
	38.0		22.50
Mean value.....			23.00

a zero slope. Actually the angles were calculated from the diagonal line of the pure liquid phase.

The percentage calculated in this manner would not be that of the true

eutectic alloy but rather would mark the beginning of a eutectic range within which the curves are indistinguishable from that of the true eutectic range. Figure 5 (upper diagram) shows a typical alloy within the range used and the slope of the line and (lower diagram) angular slopes for all alloys containing between 12 and 20 per cent indium. Table 1 shows the results of the several calculations and the variation in individual results. The mean value of 23 per cent agrees well with the observed value of 22.7 per cent in marking the beginning of the eutectic range.

Using such a check method, the most accurate values should be obtained when the composition of the alloy lies about half way between that of a pure constituent and that of the eutectic alloy. As the percentage falls too low the curve fails to give a discernable straight-line portion (see figure 3, lower left). As the percentage approaches that of the eutectic composition too closely, the slope of the line approaches the horizontal too closely to permit of accurate measurement. Obviously, too, this method is limited to the differential curve method, which alone gives a straight-line curve for the pure phase, and to cases where the flattening of the curve during phase change is sufficient to yield a straight line the slope of which can be measured. It was found that the indium-rich alloys did not give such curves; hence this method could not be used to determine the other end of the eutectic range.

GALLIUM-RICH ALLOYS

On the gallium side of the curve there was no evidence of the formation of solid solutions, for the alloy containing but 2 per cent indium showed a definite bulge at the eutectic temperature of 16°C. (see figure 3). The alloy containing 1 per cent indium showed a similar though less pronounced bulge. Any solid solution formed must, therefore, contain less than 1 per cent indium. Like gallium itself, the gallium-rich alloys have a marked tendency toward supercooling. In spite of the fact that the eutectic alloy freezes normally at 16°C., it was possible to maintain some of these alloys in a liquid state at temperatures several degrees below 0°C. As was previously noted, this necessitated the use of melting curves in place of the more common cooling curves and made it more difficult to determine accurately points on the liquidus curve. Figures 3 and 4 show melting curves for several typical gallium-rich alloys.

INDIUM-RICH ALLOYS

The indium-rich alloys were studied in a manner similar to that used with the gallium-rich alloys, but fewer alloys were necessary to establish the liquidus and solidus curves. Since there was no supercooling, both melting and cooling curves were used. It was thus possible to determine points on the liquidus curve with a higher degree of accuracy than in the

case of gallium-rich alloys. It was found that gallium forms solid solutions in indium, such alloys containing up to 9.5 per cent gallium by weight. Beyond this, the eutectic alloy consisting of α -indium (solid solution of gallium in indium) and gallium appears. Figure 6 shows the cooling and melting curves for alloys containing 9 and 10 per cent of indium, together with other examples in the indium-rich range.

THE SYSTEM GALLIUM-INDIUM

Figure 7 shows the complete constitution diagram for the system gallium-indium based on the data obtained in the study of some forty distinct alloys covering the range from pure gallium to pure indium. The eutectic temperature is $16^{\circ}\text{C}.$, and the eutectic composition consists of 24 ± 0.5

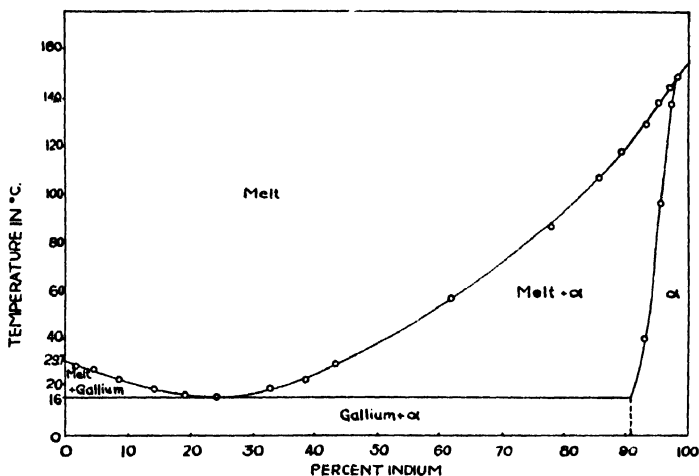


FIG. 7. Constitution diagram of gallium-indium system

per cent indium and 76 ± 0.5 per cent gallium. The solid solution range of indium in gallium is zero (or less than 1 per cent), while the solid solution range of gallium in indium extends up to 9.5 per cent gallium by weight.

CORRELATION OF RESULTS WITH THE HUME-ROTHERY THEORY OF SOLID SOLUTION PROBABILITY

According to the theory developed by Hume-Rothery, the range of solid solution of one metal in another is determined largely (other factors such as valence and crystal structure being somewhat similar) by the relative atomic (or ionic) radii of the constituent metal atoms. Where the difference in atomic radii is slight, the probability of solid solutions is high. Where the difference is greater than 13.5 per cent, the probability of solid solutions is low. Within the range 0 to 13.5 per cent, the amount of solid

solution formed might be expected to vary inversely with the increase in percentage difference in the atomic radii of the constituent metals.

If we take the Goldschmidt values of 3.14 A.U. and 2.75 A.U. for the radii of the indium and gallium atoms, respectively, we find a mean difference in radius of 13.3 per cent. This would indicate the probability of limited or border-line solid solutions in the system. It is evident that the results predicted by the Hume-Rothery rule are in qualitative agreement with the observed results. On the other hand, the use of other obtainable values for atomic radii all indicate the probability of no solid solutions, for in all such cases the mean difference in atomic radii is greater than the limiting value of 13.5 per cent.

FLUIDITIES AND CHANGES IN VOLUME OF THE BINARY SYSTEMS ISOPROPYL ALCOHOL-BENZENE AND ISOPROPYL ALCOHOL-WATER¹

ALLEN L. OLSEN² AND E. ROGER WASHBURN

Avery Laboratory of Chemistry, University of Nebraska, Lincoln, Nebraska

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The extension of the laws governing dilute solutions to a variety of components in concentrated solutions has attracted considerable attention in recent investigations. A critical scrutiny of the derived equations, which are thermodynamically sound and which in a measure have correlated changes in colligative properties with changes in concentration, reveals that these were deduced for ideal mixtures containing one component greatly in excess of the other.

The applications of the generalizations of van't Hoff, Raoult, and Henry to property-composition relations have been the subjects of many research problems. These are problems of great importance, from both theoretical and practical standpoints, and much of physical chemistry is concerned with them.

The problem of solubility may be considered from two angles. In the first place, one may consider how the escaping tendency of any component of a solution varies with the composition of the solution, and in the second place, one may consider how this escaping tendency depends upon the specific character of the components.

As a part of a comparative study of binary and ternary systems made up of water, a hydrocarbon, and a lower alcohol, the following observations have been made on solutions of isopropyl alcohol in benzene and isopropyl alcohol in water.

MATERIALS

The methods of purification and the physical constants of these materials have been discussed and recorded in a previous article (10).

¹ Presented at the Mid-West Sectional Meeting of the American Chemical Society, held at Omaha, Nebraska, April 29-May 1, 1937.

² Present address: Department of Chemistry, Kansas State College, Manhattan, Kansas.

EXPERIMENTAL

Viscosity

The viscosities of alcohol-water and alcohol-benzene systems were determined with a modification of the Ostwald viscometer designed to

TABLE 1

Fluidity-composition and change in volume for the system isopropyl alcohol-benzene

PER CENT ALCOHOL		SPECIFIC VOLUME			FLUIDITY			$K\Delta V$ ($K = 1700$)	CHANGE IN VOLUME EXPANSION IN PER CENT
By weight	By volume	V (Ob- served)	V (Calcu- lated by equation 1)	V (Calcu- lated by equation 4)	ϕ (Ob- served)	ϕ (Cor- rected by equa- tion 9')	ϕ (Theo- retical, equa- tion 10)		
00.00	00.00	1.1445	1.1445	1.1445	165.5	165.5	165.5	0.0	0.00
8.99	9.95	1.1593	1.1567	1.1580	167.0	164.8	153.8	2.2	0.21
18.36	20.10	1.1736	1.1695	1.1719	165.1	161.0	141.9	4.1	0.36
27.33	29.61	1.1846	1.1817	1.1848	154.4	150.0	130.7	5.4	0.39
37.42	40.08	1.2000	1.1954	1.1990	142.0	135.9	118.4	6.1	0.38
47.06	49.86	1.2124	1.2085	1.2124	128.2	121.6	106.9	6.6	0.31
57.53	60.25	1.2260	1.2224	1.2266	111.9	104.8	94.7	7.1	0.27
67.90	70.30	1.2393	1.2359	1.2402	94.0	86.7	82.9	7.3	0.19
78.69	80.51	1.2531	1.2516	1.2543	76.9	72.3	71.9	4.6	0.13
89.22	90.25	1.2665	1.2650	1.2673	62.8	58.9	59.5	3.9	0.05
100.00	100.00	1.2806	1.2806	1.2806	48.0	48.0	48.0	0.0	0.00

Equation 9' is $\phi = \varphi - K\Delta V$.

TABLE 2

Fluidity-composition and change in volume of the system isopropyl alcohol-water

PER CENT ALCOHOL		SPECIFIC VOLUME			FLUIDITY			$K\Delta V$ ($K = 1700$)	CHANGE IN VOLUME CONTRAC- TION IN PER CENT
By weight	By volume	V (Ob- served)	V (Calcu- lated by equation 1)	V (Calcu- lated by equation 4)	ϕ (Ob- served)	ϕ (Cor- rected by equa- tion 9)	ϕ (Theo- retical, equation 10)		
00.00	0.00	1.0029	1.0029	1.0029	111.74	111.74	111.74	0.0	0.00
7.85	9.80	1.0164	1.0245	1.0300	78.0	87.4	105.5	9.4	0.80
14.95	18.32	1.0262	1.0442	1.0536	57.9	73.9	100.1	16.0	1.73
25.20	30.06	1.0440	1.0727	1.0861	43.1	65.9	92.6	22.8	2.68
33.93	39.60	1.0640	1.0969	1.1126	36.1	62.8	86.5	26.7	3.01
44.08	50.14	1.0909	1.1250	1.1418	33.2	61.8	79.8	28.6	3.03
53.97	59.94	1.1194	1.1524	1.1683	32.3	59.3	73.5	27.0	2.87
64.81	70.15	1.1528	1.1825	1.1973	33.2	58.4	67.0	25.2	2.48
75.83	80.01	1.1884	1.2130	1.2245	36.9	56.5	60.7	19.6	2.03
87.51	89.94	1.2297	1.2454	1.2515	42.9	53.3	54.3	10.4	1.27
100.00	100.00	1.2801	1.2801	1.2801	48.0	48.0	48.0	0.0	0.00

prevent evaporation, and the usual procedures were observed (4). The viscometer was suspended in a thermostatically controlled water bath, kept at 25.00°C.

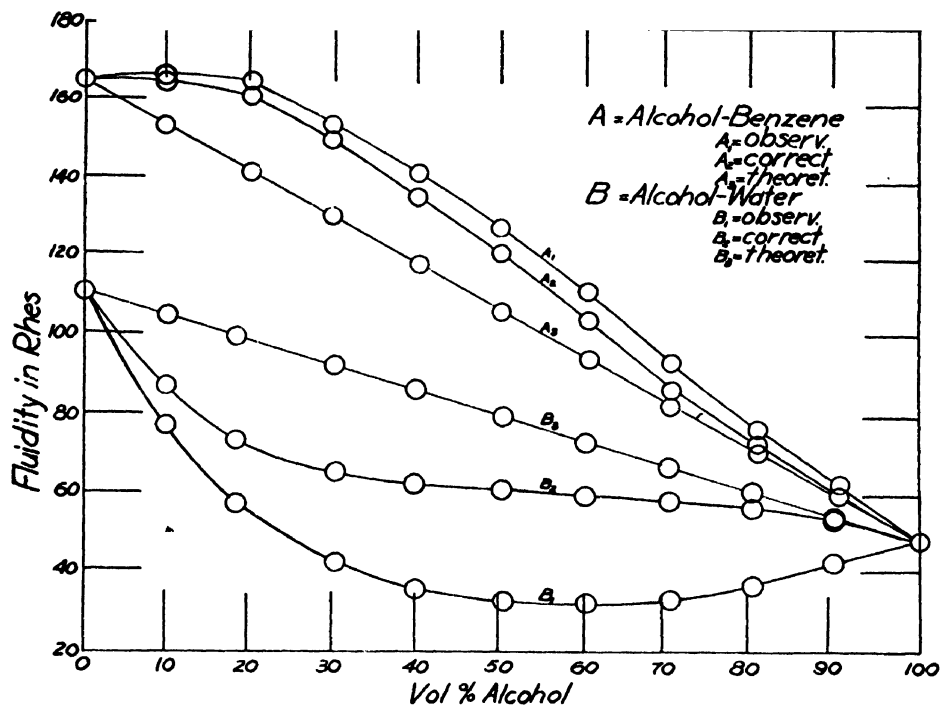


FIG. 1. Fluidity curves for isopropyl alcohol-benzene and isopropyl alcohol-water systems

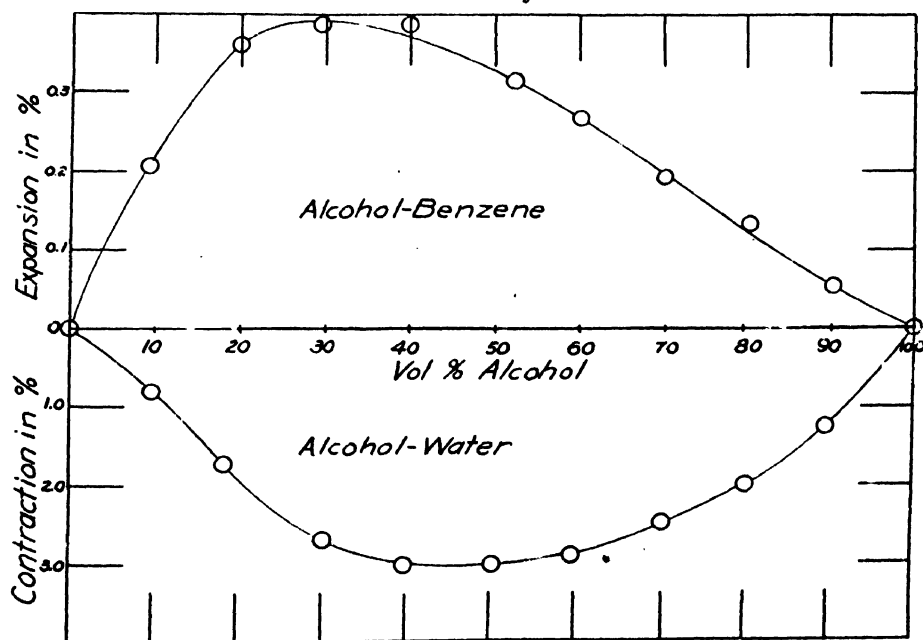


FIG. 2. Change in volume curves for isopropyl alcohol-benzene and isopropyl alcohol-water systems

The viscosities were calculated relative to water as unity at the same temperature. The fluidity of water at 25.00°C. was taken as 111.74 rhes, the value calculated from viscosity data given by the International Critical Tables (7). The product of this value and the reciprocal of the viscosity value gave the fluidity for each respective determination. The method of calculating the theoretical and corrected fluidities and the nomenclature followed in recording the data are those given by Bingham and Brown (3).

Equation 1	$V = mV_1 + nV_2$	a and b = volume fractions
Equation 4	$V = aV_1 + bV_2$	m and n = weight fractions
Equation 9	$\phi = \varphi + K\Delta V$	V_1 and V_2 = specific volumes
Equation 10	$\phi = a\varphi_1 + b\varphi_2$	ϕ = volume-corrected fluidity φ = fluidity

$K = 1700$ = fluidity when the free volume is unity

The fluidity-composition data are recorded in tables 1 and 2 and are plotted on figure 1. In the first two columns of the tables the weight and volume concentrations of the first component are given. In the third column are given the observed specific volumes, in the fourth column are the specific volumes calculated by equation 1, and in the fifth column there are given for comparative purposes the specific volumes which would be expected by equation 4, if the specific volumes were a linear function of the volume concentration. The difference between columns four and five multiplied by 1700 gives the value in column 9, i.e., $K\Delta V$. The observed fluidity is given in column 7, while the volume-corrected fluidities immediately derived from them by equation 9 are also regarded as observed and are given in column 7. If an expansion in volume accompanies the mixing of a pair of liquids, the value in column 9 must be subtracted from the observed fluidity in column 6; this is the case with the isopropyl alcohol-benzene system.

Change in volume

The weights and densities of the components and the densities of the liquid mixtures of the two binary systems provided one with the necessary data with which to calculate the change in volume accompanying the mixing process. The method of calculation was that given by Washburn (12).

The data for the changes in volume are given in column 10 in tables 1 and 2 and are plotted on figure 2.

DISCUSSION

From a consideration of internal pressures (5) and dielectric constants (8) one might arrange these liquids in order of their decreasing polarities: water \gg isopropyl alcohol $>$ benzene, \gg indicating the rather high polarity of water itself. On the basis of polarity measurements, the alcohol

and water, which have high dielectric constants, are termed polar, and the hydrocarbon with a low dielectric constant is termed non-polar. There is no sharp distinction between the two classes, since one class gradually merges into the other. The fundamental distinction between the normal (non-polar) and associated (polar) lies in the greater symmetry of the fields of force surrounding the molecules of the former, the field surrounding the latter being unsymmetrical or polar.

Isopropyl alcohol-benzene

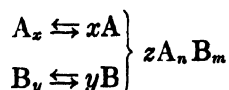
From Hildebrand's concept of solubility (6), an ideal solution is defined as one in which Raoult's law is obeyed at all temperatures and pressures.

The alcohol-benzene system deviates in a positive manner from Raoult's law. The polar molecules of alcohol have an abnormally great attraction for each other, producing greater surface tension, cohesion, etc., and tend to "squeeze" out non-polar molecules from their midst. As a result of the tendency of a liquid of high internal pressure to "squeeze" out a liquid of low internal pressure, it is expected that the partial pressure would deviate in a positive manner from Raoult's law.

This concept of association does not admit any definite polymers like double molecules. The polar affinities act within the liquid to form groups of molecules which become impregnable to a non-polar molecule like benzene.

Bancroft (1, 2) stated that he believed the disturbing factor in the solution was the tendency to form liquid layers. Bancroft calculated from positive deviations from Raoult's law for the system ethyl alcohol-benzene that, in order to explain this phenomenon, polymers of both benzene and alcohol would have to be assumed; in fact, a polymer of six molecules of alcohol and eight molecules of benzene would have to be assumed. If the polarities of the two components are sufficiently different, immiscible layers will be formed, and it is found that the greater the difference in polarity, the greater is the deviation from Raoult's law. The tendency to separate into two liquid layers is a measure of the deviation from Raoult's law.

In the study of volume change with the corresponding change in temperature, Madgin, Peel, and Briscoe (9) advance the idea that the following equilibria may exist:



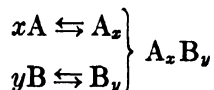
where A_z and xA represent associated molecules and simple molecules in pure liquid A, and B_y and yB represent the same in pure liquid B. $zA_n B_m$ represents a compound molecule formed from A and B. If the dissocia-

tion to simple molecules is accompanied by a drop in temperature and if the observed volume depends upon the relative number of simple, complex, and compound molecules, then the expansion in volume and a drop in temperature favor a concept of partial dissociation. There is no evidence that benzene, a non-polar liquid, is associated, whereas alcohol gives evidence of polymerization. These concepts are directly in line with the observed measurements, for in the binary mixture it is observed that there is a positive deviation from Raoult's law (11), a maximum in fluidity, an expansion in volume, a drop in temperature, and a normal freezing depression at small concentrations of alcohol (10).

Isopropyl alcohol-water

The polarities of water and isopropyl alcohol are sufficiently alike for the liquids to be miscible in all proportions. The high polarities of the alcohol and water give some measure as to the degree of association. A negative heat of dilution, a contraction in volume, a normal freezing-point depression, and a minimum in fluidity are indicative of a smaller number of molecules.

On the assumption that a greater affinity gives rise to larger complexes, the system of molecules becomes



causing the smaller particles to become associated with the possibility of a union to $A_x B_y$. The shift in equilibrium results in an evolution of heat and a contraction in volume. If an associated molecule of alcohol and an associated molecule of water united to form a loose aggregate of $A_x B_y$, the free space would be diminished, thereby resulting in a decreased fluidity. Such a union, providing the correct relation in fractional removal of molecules took place, would result in a normal freezing-point depression.

SUMMARY

1. The fluidities of the isopropyl alcohol-benzene and isopropyl alcohol-water systems have been measured.
2. The changes in volume of isopropyl alcohol-benzene and isopropyl alcohol-water throughout the entire range have been calculated.
3. Attempts have been made to correlate the physicochemical properties of these systems.

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STUDY OF ELECTROLYSIS OF METALLIC PERCHLORATES IN CELLOSOLVE¹

JOHN L. BEAL AND CHARLES A. MANN

Division of Chemical Engineering, University of Minnesota, Minneapolis, Minnesota

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The study of the electrolysis of solutions of metallic perchlorates in organic solvents conducted by Mann and Chaney.⁽¹⁾ showed that in general these salts are very highly soluble, that their solutions in the monoethyl ether of ethylene glycol are of relatively high conductivity, and that from them many metallic elements can be electrodeposited.

It is well known that from anhydrous solutions in organic solvents it is possible to electrodeposit some of the metals which are too reactive to be deposited from aqueous solutions. The alkalis and alkaline earths have been deposited from their halides and thiocyanates in alcohol, in acetone, or in pyridine solution. Patten and Mott (13, 14, 15, 16) and Müller and his associates (7 to 12) have investigated the electrolysis of many inorganic salts in common organic solvents by determining cathodic polarization curves, i.e., curves showing the influence of current density upon cathode potential. From the forms of these curves and the values of the potentials they were able to observe the electrodeposition of metals even though they were so reactive that it was difficult to confirm the deposition by chemical analysis after the cathode had been removed from the cell and freed from its solution.

During the course of the investigation by Mann and Chaney some evidence was obtained which indicated that aluminum might be electrodeposited from the solution of its perchlorate in the monoethyl ether of ethylene glycol. The scarcity of solutions, other than fused salts, from which aluminum can be deposited made this of interest. It was thought well to investigate deposition from this solvent further by using the polarization curve method of Patten and Mott and of Müller. This paper presents these results. In addition, the dielectric constant of the monoethyl ether of ethylene glycol and the conductivities of solutions of salts in it, even highly concentrated solutions, are reported.

MATERIALS

The monoethyl ether of ethylene glycol was obtained from the Carbide and Carbon Chemicals Corporation under the trade name of Cellosolve.

¹ Submitted by John L. Beal to the Graduate School of the University of Minnesota in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

It was dried with soluble anhydrite (5), filtered, and vacuum-distilled from fresh turnings of metallic calcium. Fractionation with a 90-cm. packed column and discarding of the initial product gave a constant-boiling fraction whose boiling point at 738 mm. was 133.8°C. By use of the manufacturer's vapor pressure-temperature chart this was corrected to 134.7°C. at standard pressure. Solvent purified in this manner had a conductivity as low as 9.3×10^{-8} reciprocal ohms. Its physical properties are given in the literature (17).

Silver perchlorate was prepared from silver oxide and 70 per cent perchloric acid. The silver oxide was obtained by treating silver nitrate with sodium hydroxide. After two recrystallizations the silver perchlorate was evaporated to dryness on a water bath and then further dried in a flask heated to 125–130°C., through which dry purified air was drawn. The salt so obtained showed 52.02 per cent of silver as compared with the theoretical value of 52.03 per cent. Since it is very hygroscopic it was heated to above 100°C. after each time that it had been exposed to the atmosphere.

Barium perchlorate was prepared by the method of Willard and Smith (18, 19). It was dried at 250°C. in a current of dry air. By analysis it contained 40.83 per cent of barium as compared with the theoretical value of 40.85 per cent.

Lead perchlorate was prepared from white lead and 70 per cent perchloric acid. After two recrystallizations as the trihydrate any excess acid was steamed out by the method of Willard and Kassner (20). It was dried at 160°C. in a current of dry air, and was found to contain 51.01 percent of lead as compared with the theoretical value of 51.02 per cent.

Zinc perchlorate was obtained from the G. Frederick Smith Chemical Co. of Columbus, Ohio, as the hexahydrate. The anhydrous salt is not known.

Aluminum perchlorate in the anhydrous form is not known. All attempts to dry the hydrated salt by heat and vacuum led to decomposition, and drying agents, such as phosphorus pentoxide, do not remove the moisture. An electrolytic method of preparation of anhydrous solutions in the monoethyl ether of ethylene glycol is reported by Mann and Chaney (1). This consists in electrolyzing a solution of lead perchlorate in the solvent using an aluminum anode and a lead cathode, the electric current causing the replacement of the dissolved lead by aluminum from the anode. Preparation of such solutions was attempted by this method, but decomposition was indicated by the presence of traces of chlorides in the resulting solutions.

An alternative method for the preparation of solutions of aluminum perchlorate was devised which depends upon the replacement of silver from an anhydrous silver perchlorate solution by contact with aluminum

activated with mercury. This is a very slow process and several months are required for its completion. The solution remains colorless, chlorides are absent, and the solvent, after removal by evaporation in a vacuum, is of unchanged boiling point. A solution made from 20 g. of silver perchlorate and 50 cc. of solvent in contact with an excess of granular amalgamated aluminum for thirteen months was found to contain no silver and the number of equivalents of aluminum was the same, within the limits of experimental error, as that of the perchlorate. This solution was used in the polarization measurements.

DIELECTRIC CONSTANT OF THE MONOETHYL ETHER OF ETHYLENE GLYCOL

The dielectric constant of the monoethyl ether of ethylene glycol was determined by means of a capacity bridge supplied with alternating current of approximately 3500 frequency and tuned to the point of balance with two stage amplified ear phones. One arm of the bridge, figure 1, contained two fixed condensers, C_1 and C_2 , each of 200 $\mu\mu f$ capacity. The other arm contained a variable air condenser, C_3 , of approximately 400 $\mu\mu f$ capacity with a sensitive vernier. The two variable air condensers, C_4 and C_5 , in parallel were of 375 $\mu\mu f$ and 35 $\mu\mu f$ capacity. These latter two alone required calibration, and only the ratio of their capacities at one setting to that at any other was needed. This calibration was accomplished by comparison with a small fixed condenser.

The alternating current was supplied by the oscillator using a 171A tube in a circuit similar to the one described by Jones and Josephs (6). Its transformer consisted of three inductances,— L_1 of 700 turns of No. 28 enameled wire, L_2 of 800 turns tapped at 350, 500, and 650, and L_3 of 100 turns, all wound on the same soft iron core but insulated from each other by several thicknesses of paper. A condenser of 0.1 μf was placed across L_1 . The power supplied to the bridge was controlled by varying the turns in L_2 by means of taps. The oscillator was shielded by a grounded copper box.

Across C_2 a variable resistance, R , was used to balance any current which leaked through the cell containing the solution. This resistance consisted of two binding posts between which pencil lines were drawn joining the posts until the proper balancing conductance was obtained.

The cell consisted of two smooth platinum electrodes 25 mm. in diameter and 1 mm. apart enclosed in a Pyrex container. By first balancing the bridge to the point of minimum sound and then placing the cell with its dielectric in parallel with condensers C_4 and C_5 and rebalancing by changing only the setting of these latter condensers, the capacity of the cell could be determined; it was equal to the change in capacity of the condensers C_4 and C_5 .

The cell was standardized by using air and benzene as two media of

known value and establishing the straight-line relation between dielectric constant and capacity. This relation was checked by measuring the constants of chloroform, ethyl bromide, and water. Measurements upon the monoethyl ether of ethylene glycol showed its dielectric constant to be 29.6 ± 0.1 . The results are shown in table 1.

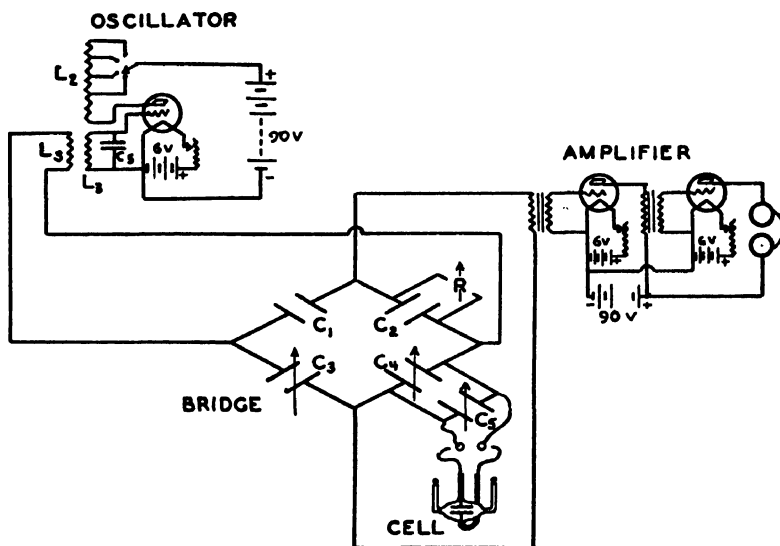


FIG. 1. Capacity bridge set-up

TABLE 1
Dielectric constants of various media

	EXPERIMENTAL D	KNOWN D^*
Air (24°C.)		1
Benzene (24°C.)		2.275
Chloroform (24°C.)	5.00 ± 0.05	4.98 ± 0.05
Ethyl bromide (24°C.)	9.80 ± 0.10	9.81 ± 0.05
Water (22°C.)	80.1 ± 0.2	79.2
Monoethyl ether of ethylene glycol (24°C.)	29.6 ± 0.1	

* International Critical Tables.

CONDUCTIVITY MEASUREMENTS

Conductivity measurements were made with a four-dial Leeds and Northrup Wheatstone bridge of the post-office type. It was supplied with alternating current by a vacuum-tube oscillator identical with that used in the previously mentioned capacity bridge except that the condenser C_5 was replaced by one of $0.11\mu f$ capacity, thereby lowering the frequency to about 900 and reducing the capacity effect in the bridge. Residual

capacity was balanced by a variable condenser placed across one of the resistances in the bridge. The Jones and Josephs method of grounding

TABLE 2
Conductance of silver perchlorate in the monoethyl ether of ethylene glycol
Cell constant = 0.3407; $R_0 = 3.55 \times 10^4$

C	R	R_c	L	A
4.5515	85.4	85.4	0.00399	0.876
4.3158	78.4	78.4	0.00435	1.008
3.690	48.9	48.9	0.00098	1.891
3.0757	39.8	39.8	0.00856	2.790
2.2308	38.7	38.7	0.00881	3.95
1.3808	46.1	46.1	0.00739	5.35
0.8961	60.9	60.9	0.00560	6.25
0.4412	99.4	99.4	0.00343	7.77
0.2078	187.2	187.2	0.001821	8.78
0.0978	344.3	344.3	0.000990	10.13
0.04607	645.0	645.0	0.000529	11.50
0.009506	2,434	2,435	0.00001400	14.72
0.002162	8,024	8,041	0.0000424	19.59
0.000536	25,080	25,250	0.00001350	25.15
0.0001132	93,950	96,350	0.00000354	31.25
0.0000346	288,000	313,600	0.000001089	31.42

TABLE 3
Conductance of barium perchlorate in the monoethyl ether of ethylene glycol
Cell constant = 0.3527; $R_0 = 3.79 \times 10^4$

C	R_c	L	A
1.2422	118.4	0.00298	2.40
0.930	129.4	0.00272	2.92
0.735	153.0	0.002305	3.06
0.6301	190.0	0.001858	2.95
0.420	305	0.001158	2.75
0.2835	473	0.000746	2.635
0.0749	1,520	0.000232	3.10
0.01980	4,132	0.0000854	4.31
0.00523	10,890	0.0000324	6.20
5.613	323.6	0.001086	0.1935
2.542	130.1	0.00271	1.067
1.112	120.5	0.00293	2.635
0.504	243.2	0.001451	2.880
0.230	575.4	0.000613	2.665
0.0960	1,317	0.000268	2.795
0.0256	3,380	0.0001088	4.05

(6) was used, and the head phones employed two stages of amplification. The conductivity cell consisted of two smooth platinum electrodes approximately 1 cm. in diameter and 1 cm. apart. The measurements were made

in a water bath at $25.00^\circ \pm 0.03^\circ\text{C}$. Saturated solutions of the salts were prepared and weaker solutions made by dilution.

TABLE 4
Conductance of lead perchlorate in the monoethyl ether of ethylene glycol
Cell constant = 0.3407; $R_0 = 3.66 \times 10^6$

<i>C</i>	<i>R</i>	<i>R₀</i>	<i>L</i>	Λ
5.7761			0.000914	0.1583
2.4782	85.5	85.5	0.00395	1.610
1.5627	95.1	95.1	0.00358	2.290
1.0341	123.9	123.9	0.002755	2.660
0.6203	208.0	208.0	0.001639	2.640
0.3985	342.0	342.0	0.000996	2.500
0.3270	413.0	413.0	0.000825	2.525
0.2768	491.6	491.6	0.0006935	2.500
0.2405	571.8	571.8	0.0005955	2.48
0.2120	651.4	651.4	0.000523	2.465
0.1900	729.6	729.6	0.000467	2.460
0.00781	9,827	9,823	0.0000347	4.45
0.01523	5,934	5,935	0.0000575	3.75
0.02955	3,541	3,541	0.0000962	3.26
0.05465	2,152	2,152	0.0001587	2.90
0.0944	1,354	1,354	0.0002515	2.665
0.1257	1,027	1,027	0.000332	2.665
1.098	123.3	123.3	0.002880	2.622
0.740	172.3	172.3	0.001975	2.67
0.667	118.2	118.2	0.00181	2.71
0.0001297	189,000	200,000	0.00000170	13.10
0.000381	87,900	90,000	0.00000379	9.95
0.000741	54,180	55,000	0.00000620	8.36
0.001803	27,700	27,900	0.00001222	6.78
0.0000485	389,000	435,000	0.000000785	16.21
0.0000252	638,000	773,000	0.000000441	17.51

TABLE 5
Solubilities of silver, barium, and lead perchlorates in the monoethyl ether of ethylene glycol at 25°C.

	SILVER PERCHLORATE	BARIUM PERCHLORATE	LEAD PERCHLORATE
Solvent density.....	0.9252	0.9252	0.9252
Solution density.....	1.688	1.645	1.630
Grams per 100 g. of solvent.....	127.65	138.20	259.4
Grams per 100 cc. of solution.....	94.36	95.162	117.29
Grams per 100 cc. of solvent.....	117.71	127.5	239.27
Normality.....	4.5515	5.660	5.7733

The results are given in tables 2 to 5 and in figure 2. In these *C* is the normality, *L* the specific conductivity of the solution in reciprocal ohms

per cubic centimeter, and Λ is the equivalent conductivity calculated by the formula

$$\Lambda = 1000 \frac{L}{C}$$

R_0 is the resistance of the cell filled with pure solvent, R the resistance of the cell filled with the solution, and R_c the corrected resistance, all resistances in ohms. The corrected resistance is obtained by applying the solvent correction (2).

$$\frac{1}{R} = \frac{1}{R_c} + \frac{1}{R_0}$$

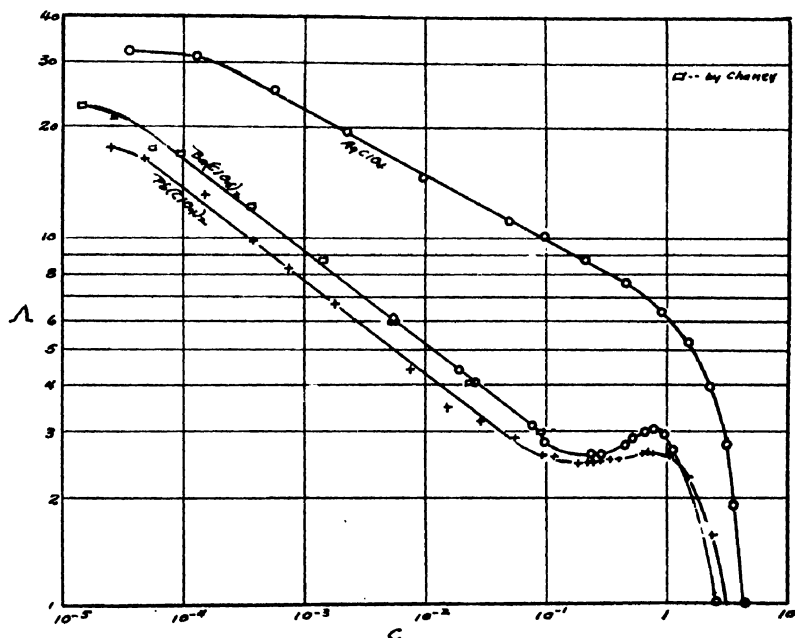


FIG. 2. Conductance curves

Figure 2, a plot of equivalent conductance and normality on log-log paper, shows that over the greater part of the concentration range the values fall in straight lines.

POLARIZATION MEASUREMENTS

Polarization measurements require the use of a reference half-cell electrode, and for non-aqueous studies it seems advisable that this electrode should employ the same solvent as the system studied. A half-cell consisting of a silver wire, the surface freshly deposited from a silver cyanide plating bath, dipped in a 0.1 *N* solution of silver perchlorate in the mono-

ethyl ether of ethylene glycol was found satisfactory. Measured against a tenth-normal calomel electrode this had a potential of -0.45 volt with respect to the calomel electrode. This corresponds to -0.78 volt with respect to a normal hydrogen electrode. The potential remained constant for several days. Figure 4 shows that the potential of silver in this solution is independent of the current density.

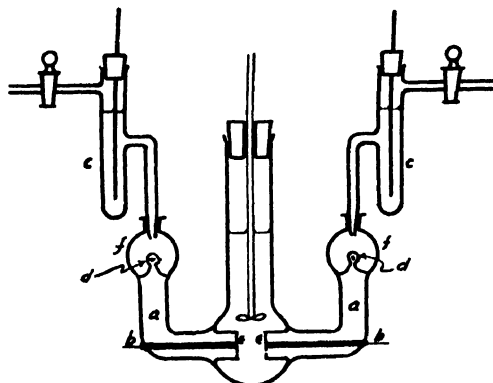


FIG. 3. Polarization cell No. I

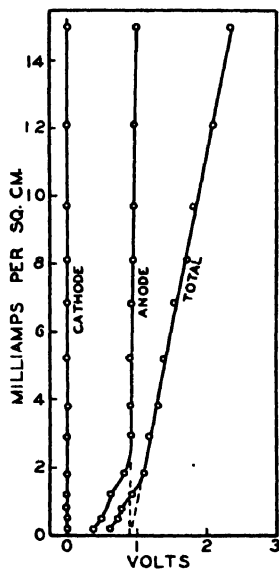


FIG. 4. Polarization curves of $0.1\ N$ silver perchlorate

The cell used was similar to that of Müller (7 to 12) except that the electrodes, e of figure 3, were 11 mm. in diameter. Communication between the solution and the half-cell electrodes, c, was made by means of small holes in each of the platinum electrodes, and diffusion was reduced by the constrictions, d, filled with glass wool. A small stirring paddle was

placed slightly above the level of the electrodes, for it was found to aid the constancy of the readings. The potential readings were taken after a

TABLE 6
Polarization measurements of 0.1 N silver perchlorate

TOTAL VOLTAGE	CURRENT DENSITY	ANODE POTENTIAL REFERRED TO Ag 0.1 N AgClO ₄ HALF-CELL	CATHODE POTENTIAL REFERRED TO Ag 0.1 N AgClO ₄ HALF-CELL
volts	milliamperes per square centimeter	volts	volts
0.61	0.020	0.38	0
0.72	0.050	0.49	0
0.78	0.081	0.63	0
0.92	0.121	0.82	0
1.10	0.183	0.91	0
1.18	0.295	0.91	0
1.30	0.381	0.92	0
1.40	0.520	0.92	0
1.54	0.685	0.93	0
1.73	0.813	0.94	0
1.80	0.870	0.94	0
2.10	1.21	0.97	0
2.33	1.50	0.99	0

TABLE 7
Polarization measurements of 1.0 N silver perchlorate

TOTAL VOLTAGE	CURRENT DENSITY	ANODE POTENTIAL REFERRED TO Ag 0.1 N AgClO ₄ HALF-CELL	CATHODE POTENTIAL REFERRED TO Ag 0.1 N AgClO ₄ HALF-CELL
volts	milliamperes per square centimeter	volts	volts
0.53	0.05	0.37	0.04
0.68	0.101	0.60	0.04
0.81	0.186	0.76	0.04
0.90	0.302	0.86	0.04
0.93	0.672	0.88	0.04
1.01	0.91	0.90	0.04
1.10	1.42	0.92	0.04
1.18	2.06	0.96	0.04
1.44	3.23	1.02	0.04
1.60	4.45	1.15	0.04
1.87	6.64	1.16	0.04
2.25	8.26	1.34	0.04
2.50	9.73	1.40	0.04
2.75	12.32	1.52	0.04

2-min. flow of current at the desired intensity. Between each reading the electrolysis was interrupted for 2 min.

Potentials were recorded by means of a vacuum-tube potentiometer as

described by Mann and Chaney (1). The leads were so arranged that the potential differences between each electrode and its reference half-cell and also between the two electrodes themselves could be quickly taken.

The electrodeposition of the noble metal silver is illustrated by tables 6 and 7 and figures 4 and 5, which refer to 0.1 and 1.0 *N* silver perchlorate in the monoethyl ether of ethylene glycol, respectively. The anode and cathode potentials are referred to the $\text{Ag}|0.1\text{ }N\text{ AgClO}_4$ half-cell. Even to the lowest values of current density the cathode potentials remain constant. It is apparent that the ratio of the activity of silver in the 1.0 *N* solution to that in the 0.1 *N* solution for the E.M.F. difference is only 0.04 rather than 0.058 volt. The difference between the anode and cathode potentials as measured by the reference electrodes, 0.90 volt and 0.81 volt for the 0.1 *N* and 1.0 *N* solutions, respectively, is in good agreement with

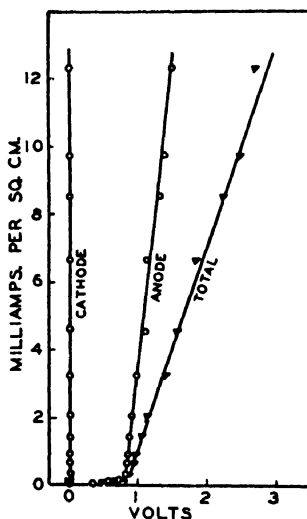


FIG. 5. Polarization curves of 1.0 *N* silver perchlorate

the decomposition voltages obtained by extrapolating the total voltage curves to zero current density. The latter values are 0.90 volt and 0.84 volt and are the voltages across the two cell electrodes. The silver deposited upon the cathode in a smooth even coat.

By addition of + 0.78 volt to the cathode potential, the potential can be referred to the hydrogen electrode except for the possible interference of liquid-junction potentials entering into the measurement of the potential of the $\text{Ag}|0.1\text{ }N\text{ AgClO}_4$ half-cell electrode against the calomel electrode. Adding this value to the potential of silver in 1.0 *N* solution gives 0.82 volt, which is at least in close agreement with the normal potential of silver, 0.80 volt, on the hydrogen scale.

The electrolysis of a 0.5 *N* solution of lead perchlorate is shown by table 8 and figure 6. It proceeded quite similarly to that of silver perchlorate.

TABLE 8

Polarization measurements of 0.5 N lead perchlorate

TOTAL VOLTAGE	CURRENT DENSITY	ANODE POTENTIAL REFERRED TO Ag 0.1 N AgClO ₄ HALF-CELL	CATHODE POTENTIAL REFERRED TO Ag 0.1 N AgClO ₄ HALF-CELL
volts	milliamperes per square centimeter	volts	volts
0.47		0.19	-0.36
0.61		0.26	-0.38
0.94		0.37	-0.52
1.08		0.41	-0.61
1.28	0.020	0.55	-0.79
1.38	0.040	0.60	-0.79
1.55	0.073	0.76	-0.79
1.66	0.097	0.82	-0.80
1.72	0.109	0.83	-0.79
1.80	0.191	0.81	-0.79
1.85	0.273	0.85	-0.80
1.90	0.387	0.84	-0.79
2.09	0.563	0.85	-0.79
2.38	0.815	0.85	-0.80
2.35	1.08	0.85	-0.80
2.60	1.28	0.90	-0.80
2.76	1.48	0.90	-0.80
	5.16	0.93	-0.80
	9.29	0.94	-0.80

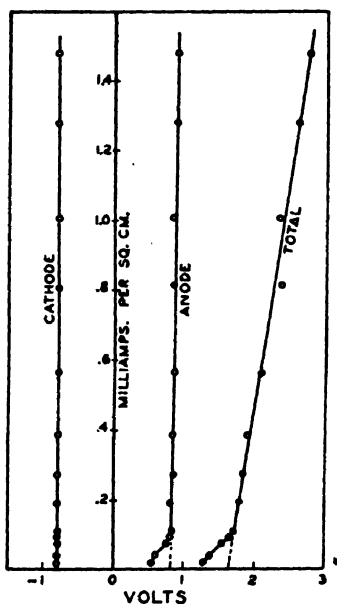


FIG. 6. Polarization curves of lead perchlorate

The sum of the individual electrode potentials agreed quite closely with the decomposition potential of the solution as obtained by extrapolation of the total voltage curve. The lead deposited in a smooth coat and its potential was -0.80 volt referred to the $0.1\text{ }N\text{ AgClO}_4\text{-Ag}$ reference electrode. Converting this to the hydrogen scale by adding 0.78 yields a value of -0.02 volt, not greatly less negative than the value $+0.09$ volt for an aqueous solution of $0.5\text{ }N$ activity.

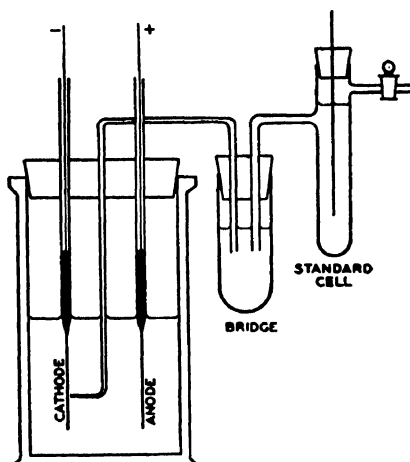


FIG. 7. Polarization cell No. I

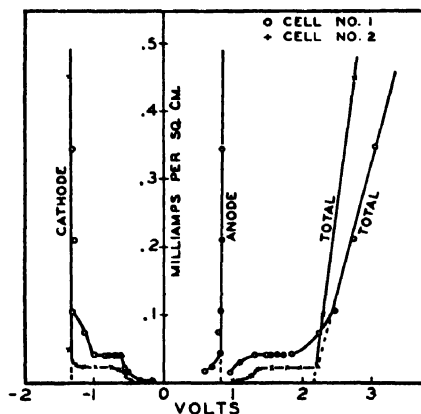


FIG. 8. Polarization curves of zinc perchlorate

The polarization curves for zinc in zinc perchlorate solution are given in table 9 and table 10 and in figure 8. These curves were obtained in two different types of cells. Cell No. I was the one already described. Cell No. II consisted of two platinum electrodes dipping beneath the solution in an open beaker and with the half-cell electrode arm pulled out to a small tip which rested very lightly upon the cathode surface as shown

TABLE 9
Polarization measurements of 0.5 N zinc perchlorate
Cell No. I

TOTAL VOLTAGE	CURRENT DENSITY	ANODE POTENTIAL REFERRED TO Ag 0.1 N AgClO ₄ HALF-CELL	CATHODE POTENTIAL REFERRED TO Ag 0.1 N AgClO ₄ HALF-CELL
volts	milliamperes per square centimeter	volts	volts
0.68	0.0053		
0.95	0.016	0.58	-0.48
1.10	0.021	0.70	-0.56
1.32	0.042	0.84	-0.63
1.46	0.042	0.84	-0.67
1.53	0.042	0.84	-0.71
1.61	0.042	0.84	-0.80
1.70	0.042	0.84	-0.85
1.82	0.042	0.84	-0.98
2.22	0.074	0.84	-1.12
2.45	0.105	0.83	-1.31
2.73	0.211	0.85	-1.28
3.02	0.348	0.85	-1.32
3.80	2.59	0.88	-1.35

TABLE 10
Polarization measurements of 0.5 N zinc perchlorate
Cell No. II

TOTAL VOLTAGE	CURRENT DENSITY	CATHODE POTENTIAL REFERRED TO Ag 0.1 N AgClO ₄ HALF-CELL
volts	milliamperes per square centimeter	volts
0.02		-0.1
0.162		-0.08
0.323		-0.08
0.485		-0.10
0.625	0.0025	-0.162
0.815	0.0025	-0.335
0.99	0.0037	-0.485
1.265	0.010	-0.550
1.36	0.020	-0.645
1.550	0.0237	-0.760
1.755	0.0237	-0.975
1.965	0.0237	-1.145
2.205	0.0262	-1.320
2.320	0.100	-1.360
2.740	0.45	-1.360
3.03	1.41	-1.360
3.84	4.75	-1.40
4.60	7.50	-1.40

in figure 7. The results from the two different cells were in excellent agreement.

Zinc is a more reactive metal than silver and lead, and the cathode potential curve is of a different nature. The potential does not immediately assume a constant value, but builds up to it as the current density is increased. According to the interpretation of Patten and Mott (13 to

TABLE 11
Polarization measurements of 1.0 N barium perchlorate
Platinum cathode

TOTAL VOLTAGE	CURRENT DENSITY	ANODE POTENTIAL REFERRED TO Ag 0.1 N AgClO ₄ HALF-CELL	CATHODE POTENTIAL REFERRED TO Ag 0.1 N AgClO ₄ HALF-CELL
volts	milliamperes per square centimeter	volts	volts
0.91	0.0051	0.25	-0.63
1.12	0.011	0.32	-0.79
1.28	0.062	0.38	-0.88
1.49	0.123	0.49	-0.94
1.53	0.122	0.51	-1.01
1.85	0.241	0.60	-1.09
2.82	0.88	0.67	-1.34
3.23	1.24	0.68	-1.42
3.57	1.55	0.67	-1.52
4.88	2.62	0.70	-1.74
	3.68	0.70	-1.93

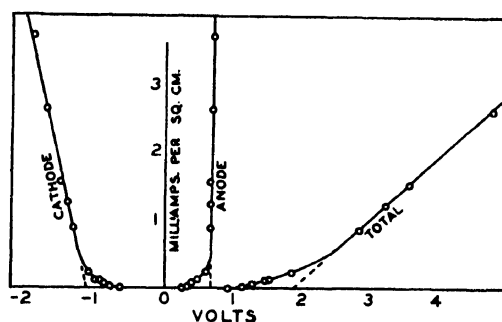


FIG. 9. Polarization curves of barium perchlorate with platinum cathode

16) and of Müller (7 to 12), the zinc reacts below the threshold value of current density, going into solution as rapidly as it is formed, and no residual amount is deposited. At higher current densities the rate of electrodeposition is greater than the rate of solution and zinc is actually deposited in a visible coat. The potential of the zinc is -1.40 volts referred to the reference electrode used, and this can be converted to -0.62 volt on the hydrogen scale.

The curves for the electrolysis of barium perchlorate between platinum electrodes are different from those of the previous metals. The cathode potential continues to increase with increasing current density, as shown in table 11 and figure 9. The cathode decomposition potential, obtained by extrapolating to zero current density, is only -1.15 volts, and this is much less negative than would be expected for the highly reactive metallic barium.

The potential of metallic barium cannot be measured directly in the solution because its reactivity prevents the keeping of a clean metallic surface. Müller, however, has employed the process of amalgamating

TABLE 12
Polarization measurements of 1.0 N barium perchlorate
Cadmium cathode

TOTAL VOLTAGE	CURRENT DENSITY	ANODE POTENTIAL REFERRED TO Ag 0.1 N AgClO ₄ HALF-CELL	CATHODE POTENTIAL REFERRED TO Ag 0.1 N AgClO ₄ HALF-CELL
<i>volts</i>	<i>milliamperes per square centimeter</i>	<i>volts</i>	<i>volts</i>
1.25	0.05	0.25	-1.02
1.42	0.09	0.35	-1.13
1.85	0.21	0.57	-1.28
2.20	0.35	0.68	-1.56
2.92	0.47	0.68	-2.03
3.35	0.49	0.68	-2.24
3.90	0.87	0.68	-2.30
4.45	1.35	0.69	-2.28
4.66	1.55	0.70	-2.28
	3.15	0.71	-2.29
	4.05	0.72	-2.30
	4.90	0.73	-2.40
	4.76	0.73	-2.46
	7.26	0.77	-2.48
	16.21	0.77	-2.48
	90.0	0.78	-2.49

reactive metals in order to obtain their potentials, and he identified a deposit as calcium by comparing its potential with that of amalgamated calcium in the same solution (9). In the 1.0 N barium perchlorate solution amalgamated barium was found to have a potential of -2.16 volts with respect to the reference half-cell electrode. This is so much more negative than the decomposition potential of the cathode that there is no possibility that barium was deposited during the electrolysis.

The barium solution was electrolyzed using metal cathodes other than platinum. These were obtained by plating the desired metal upon the cell cathode. The cathode potential curves obtained with a copper cath-

ode and with a zinc cathode were rather similar to those obtained with platinum, and the potentials were too positive to indicate the deposition of barium. The results with a cadmium cathode, given in table 12 and figure 10, do indicate the deposition of metallic barium. Above the threshold value of 0.5 milliamperes per square centimeter barium is deposited at a potential of -2.28 volts. The favorable influence of the cadmium cathode can be explained by the tendency of barium to form alloys with cadmium, as reported by Gautier (4).

Chemical confirmation of the deposition was poor, for with removable cathodes any attempts to remove the cell liquor resulted in the removal of the deposit as well, and only traces of barium could be reported. But

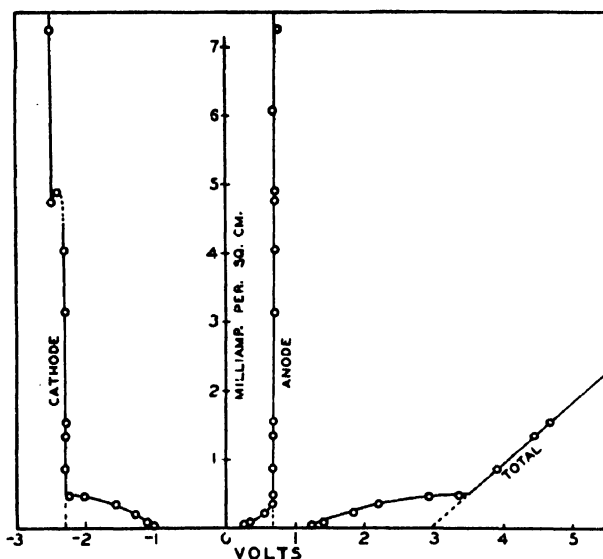


FIG. 10. Polarization curves of barium perchlorate with cadmium cathode

when the cathode was removed quickly and placed in distilled water, small amounts of hydrogen gas could be seen to be evolved.

For the deposition of aluminum one would expect copper to be a favorable cathode metal, for several compounds of copper and aluminum have been reported (3). Table 13 and figure 11 show the results of the electrolysis of a $0.5\ N$ solution of aluminum perchlorate prepared as previously described. The irregularity of the curves is similar to that found by Müller for the electrolysis of aluminum iodide in pyridine (9). No cathode potential value is negative enough to indicate the deposition of metallic aluminum. For comparative purposes the potential of aluminum was measured in the same solution. When freshly cleaned and scraped, aluminum had a potential of -0.67 volt with respect to the $0.1\ N\ AgClO_4-Ag$

TABLE 13
Polarization measurements of 0.5 N aluminum perchlorate
Copper cathode

TOTAL VOLTAGE	CURRENT DENSITY	CATHODE POTENTIAL REFERRED TO Ag 0.1 N AgClO ₄ HALF-CELL
volts	milliamperes per square centimeter	volts
0.47	0.03	-0.26
0.74	0.19	-0.35
0.77	0.25	-0.35
0.88	0.37	-0.47
0.93	0.45	-0.48
1.02	0.61	-0.60
1.06	0.74	-0.65
1.23	1.00	-0.93
1.50	1.30	-0.85
1.85	1.75	-0.80
1.95	1.95	-1.08
2.05	2.20	-1.30
2.12	2.45	-1.20
2.27	2.97	-1.15
2.38	3.85	-0.95
2.63	4.75	-0.95
3.05	5.70	-1.10
3.38	6.25	-0.79
3.85	7.70	-0.80
4.43	9.25	-1.10
4.47	11.60	-0.90

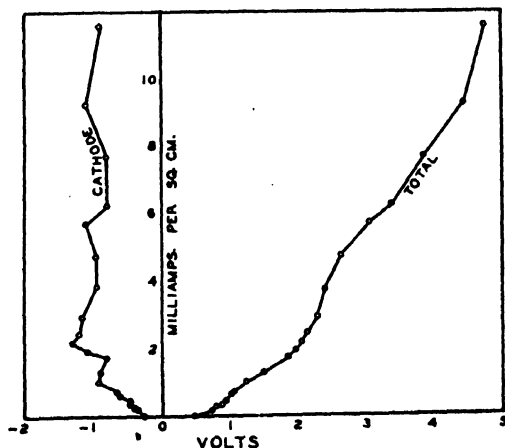


FIG. 11. Polarization curves of aluminum perchlorate

electrode. This value is obviously less negative than the true potential of the metal. Samples amalgamated by rubbing the cleaned surface with mercury had potentials ranging between -1.59 and -1.61 volts. Samples

amalgamated by dipping in aqueous mercuric chloride and drying with alcohol and ether gave potentials between -1.83 and -1.94 volts. While these values are not in agreement, they are enough more negative than the cathode potentials to indicate the absence of aluminum deposition during the electrolysis.

CONCLUSION

Both the dielectric constant of the monoethyl ether of ethylene glycol and the conductance of its solutions are between those of methyl and ethyl alcohols. The monoethyl ether of ethylene glycol may be considered as an alcohol of high molecular weight, and as such the high molecular weight does not, in this case, show the usual effect of decreasing conductance.

The polarization curves show that metals even as reactive as barium may be electrodeposited from solutions in the monoethyl ether of ethylene glycol. Although anhydrous solutions of aluminum perchlorate may be prepared in this solvent, the polarization curves show no tendency toward the electrodeposition of aluminum from such solutions.

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NEW BOOKS

Outlines of Theoretical Chemistry. By F. H. GETMAN and FARRINGTON DANIELS. Sixth edition. 662 pp. New York: John Wiley and Sons, 1937. Price: \$3.75.

Although a large amount of new material is included in the sixth edition of this well-known textbook of physical chemistry, the length of the book is practically unchanged. This result has been accomplished by means of a marked abbreviation of some of the older material, particularly of those parts which dealt with experimental methods; for example, twenty diagrams of apparatus and their attendant descriptions which were present in the fifth edition are now omitted.

It is interesting to note that the thermodynamic notation of Léwis and Randall has been adopted in the present edition.

The new material which appears in this edition includes such topics as quantum mechanics, the Hund-Mulliken theory, the Heitler-London theory, and the calculation of activation energies. While Dr. Daniels has been very skillful in his brief presentation of these relatively difficult topics, the discussion of them is necessarily purely descriptive. The reviewer is of the opinion that there is some danger that this type of treatment may give the beginning student the impression that physical chemistry, while interesting, is a rather intricate subject full of formulas whose derivations are difficult, of little interest, and certainly none of his concern. To compensate partially for this lack of rigor in the text, a sixteen-page appendix of derivations has been added, ranging in difficulty from the evaluation of van der Waals constants to a discussion of the Debye-Hückel theory. A few minor mistakes, such as the curiously impractical method for collecting radon (page 577), have found their way from the fifth to the sixth edition.

On the whole Dr. Daniels is to be congratulated on a successful revision of a valuable text. The changes will undoubtedly increase the widespread popularity which the book now enjoys.

ROBERT LIVINGSTON.

Die Fluoreszenzanalyse in der Mikrochemie. Monographien aus dem Gesamtgebiete der Mikrochemie. By MAX HAITINGER. 192 pp.; 4 fig.; 7 tables. Vienna and Leipzig: Emil Haim and Co., 1937. Price: 8 RM.

The author, who was awarded the Fritz Pregl Prize for his work in fluorescence microscopy, has in this monograph made a worthwhile contribution to the literature of fluorescence analysis. Already many important applications of this comparatively new physicochemical method of analysis have been made in the microchemical field, and doubtless the future will see more extensive development of the technique, especially, it is to be hoped, in the quantitative branch of analysis. The topics treated in the book include: light sources and filters, methods of fluorescence analysis, fluorescence microscopy, fluorometry, applications of fluorescence analysis in chemical investigations (individual tests for many inorganic and organic substances are described), mineralogical applications, trace detection, and micro reactions in animal and vegetable cells. There are more than 800 references (with titles) to the literature.

A number of typographical errors, especially in the spelling of names, were noted. At the bottom of page 52, "Mg-Oxim" is evidently a misprint for "Mg-Oxin."

E. B. SANDELL.

Gmelins Handbuch der anorganischen Chemie. 8 Auflage. Herausgegeben von der Deutschen Chemischen Gesellschaft. System-Nummer 35: Aluminium. Teil A. Lieferung 5. Legierungen von Aluminium mit Zink bis Uran. 26 x 18 cm.; pp. xvi + 683-886. Berlin: Verlag Chemie, 1937. Price: 24.75 RM.

This section continues the treatment of aluminum alloys, and further parts will follow. It deals with the alloys, simple and mixed, of aluminum with zinc, cadmium, mercury, gallium, indium, thallium, rare-earth metals, titanium, zirconium, hafnium, thorium, germanium, tin, lead, vanadium, niobium, tantalum, chromium, molybdenum, tungsten, and uranium. The treatment is on the usual lines of descriptive text, tables, and diagrams, and a wealth of information is given in an admirably concise form, with full references to the literature. In view of the increasing importance of aluminum alloys, this volume will be especially welcome.

J. R. PARTINGTON.

Magnesium-Legierungen. Patentsammlung geordnet nach Legierungssystem von A. Grützner. Zugleich Anhang zu Magnesium Teil A in *Gmelins Handbuch der anorganischen Chemie*. 8 Auflage. Herausgegeben von der Deutschen Chemischen Gesellschaft. 26 x 18 cm.; 192 pp. Berlin: Verlag Chemie, 1937. Price: 15 RM.

This volume consists entirely of tables giving the salient properties and uses of magnesium alloys with references to patents. It includes a large number of alloys of great importance in modern technology and should be invaluable not only to chemists but also to engineers. The plan of the work is clearly described in a short preface, so that the reader will be able to find any particular alloy without difficulty.

J. R. PARTINGTON.

Gmelins Handbuch der anorganischen Chemie. 8 Auflage. Herausgegeben von der Deutschen Chemischen Gesellschaft. System-Nummer 22: Kalium. Lieferung 3. 26 x 18 cm.; pp. xx + 515-804. Berlin: Verlag Chemie, 1937. Price: 35.25 RM.

This section of the volume on potassium includes compounds with bromine and iodine (including salts of oxyacids), sulfur, selenium, and tellurium (including salts of oxyacids and salts of acids of nitrogen and sulfur). The methods of preparation include technical processes in the case of salts of industrial importance. The properties are given very fully and comprise both physical and chemical properties for the solids and solutions. Among physical properties may be noticed the full discussions of crystal structure and optical properties. The colored forms of the haloid salts formed by radiation, etc., are discussed and the polybromides and polyiodides receive adequate treatment. Systems of salts are treated from the point of view of the phase rule. This volume, it will be seen, contains important and interesting material and the treatment is full and authoritative, recent literature being very satisfactorily covered.

J. R. PARTINGTON.

Gmelins Handbuch der anorganischen Chemie. 8 Auflage. Herausgegeben von der Deutschen Chemischen Gesellschaft. System-Nummer 27: Magnesium. Teil A. Lieferung 1. 26 x 18 cm.; pp. iii + 156. Berlin: Verlag Chemie, 1937. Price: 18 RM.

This is the first part of the volume on magnesium and deals with the history, occurrence, and preparation (including technical processes) of magnesium. The section on occurrence is very complete on the geological, economic, and geochemical sides, the mineral deposits in the United States receiving very ample treatment. The production of the metal is well described, the electrolysis of the fused chloride,

free from water, being the most important method. The utilization of the chlorine evolved in working up oxide or carbonate minerals is mentioned. The technical undertakings in Germany, France, the United States, and England are stated, and attention is directed to the large increase in the production of the metal in a very recent period. The total annual production has been estimated as 25,000 tons in 1935 as compared with 2500 tons in 1929 and 250 tons in 1926. This great increase is due to the increasing use of light alloys containing magnesium. The cells used for the electrolysis of the fused chloride contain a carbon anode and iron cathode, separated by a partition or diaphragm, the exact construction being little known. The electrolysis of the oxide in a bath of molten fluoride is also in use. The separation of the metal in the cell is rather difficult and in the Ashcroft process, used in England, an alloy of lead and magnesium is first obtained and afterwards separated in a second electrolytic cell. The metal may be purified by sublimation.

The information in the volume is very detailed and up-to-date; the literature has been well covered.

J. R. PARTINGTON.

Gmelins Handbuch der anorganischen Chemie. 8 Auflage. Herausgegeben von der Deutschen Chemischen Gesellschaft. System-Nummer 27: Magnesium. Teil A. Lieferung 2. 26 x 18 cm.; pp. vi + 157-372. Berlin: Verlag Chemie, 1937. Price: 25.50 RM.

This section contains the physical properties of the magnesium nucleus (including the isotopes 23, 24, 25, 26, and 27), atom, crystals, and massive metal. They are very exhaustively dealt with, the spectra, magnetism, and electrochemical relations being included. The chemical properties are given in outline, according to the usual plan of the work, and there is a good section on analysis. The preparation of this section has involved the abstraction of a large amount of literature, and very recent papers and monographs are well covered. In view of the increasing use of magnesium in metallurgy, this volume will provide indispensable information for those engaged in technical concerns as well as for the research chemist and analyst. The thorough consideration of the physical chemistry of magnesium is very noteworthy.

J. R. PARTINGTON.

Selected Topics in Colloid Chemistry. By ROSS AIKEN GORTNER. 6 x 9 in.; 169 pp.; 35 fig. Ithaca, N. Y.: Cornell University Press, 1937. Price: \$2.50.

"This book covers the content of a series of lectures delivered in the Department of Chemistry of Cornell University during the first semester of the academic year 1935-1936, at which time the author held the George Fisher Baker Non-Resident Lectureship in Chemistry." (p. vii.)

Serving as an introduction to the book is the public lecture on "Scientific Genealogy" presented by the author at the beginning of his lectureship. This is followed by eight chapters grouped under the following headings: "The Beginnings of the Science"; "What is 'Colloid Chemistry'"; "Some Basic Concepts"; "Some Fundamental Properties of Colloid Systems"; "Electrokinetics"; "Surface Tension, Surface Energy, Interfacial Tension, and Molecular Orientation"; "Adsorption"; "The Water Relationship of Bio-Colloids."

The author has treated each topic briefly but systematically, has brought the material up-to-date, and has especially emphasized the application of colloid chemistry to biochemical problems; of particular interest is his able treatment of the controversial subject "bound water." He has included, in condensed and well-oriented form, much of the highly important and extensive work from his own laboratories.

While the material presented is not intended to serve as a text in colloid chemistry, it does furnish an excellent introduction to that subject, and can be recommended to all who are interested in it. It will be of special value to the biochemist, who will find a welcome approach to the realm of colloid chemistry through the medium of examples with which he already has a speaking acquaintance.

F. E. BARTELL.

The Chemistry and Technology of Rubber. C. C. DAVIS, Editor, and J. T. BLAKE, Assistant Editor. 941 pp. New York: Reinhold Publishing Co., 1937.

This book, which is No. 74 in the series of A.C.S. Monographs, is a collection of twenty-six chapters, each written by one or more authorities in the field. The book is encyclopedic in character; the chapters cover all phases of rubber chemistry and technology from crude rubber to finished products, and from the chemistry of the rubber hydrocarbon through polymerization, vulcanization, accelerators, and auto-oxidation to synthetic and substitute rubbers. As the book was written by some forty contributors, each one an authority on some phase of the rubber problem, it would be difficult to find a reviewer who was competent to judge accurately the merits of the whole work. This reviewer has accordingly read critically only those chapters which he felt competent to judge (chapters 3, 8, 9, 12, 13, 14, and 20). These seven chapters are distinguished by clarity of presentation, thoroughness of treatment, and unbiased attitude in presenting all the facts and theories, and yet a definite critical faculty is exercised throughout. The material is up-to-date and the bibliographies are extensive. A cursory examination of the other nineteen chapters indicates that these, too, are well written and complete. The whole book is distinguished by a continuity which reflects great credit upon the editor and his assistant. The printing and binding are quite up to the standard for this series of monographs, and there is a section on the literature of the chemistry of rubber, as well as over forty pages of author and subject indexes. Altogether, this is an excellent treatise.

LEE IRVIN SMITH.

Colorimetric Methods of Analysis, Volume II, Organic and Biological. By FOSTER D. SNELL and CORNELIA T. SNELL. New York: D. Van Nostrand Co., 1937. Price: \$9.50.

Soon after the appearance of the first volume of *Colorimetric Methods of Analysis* dealing with the colorimetry and nephelometry of inorganic substances, this second volume giving similar methods for organic substances was published. Because of the great number of known organic substances, it is not possible to give an exhaustive treatment of all of them. The authors have concentrated mainly on those substances which are of importance from a biological or medical viewpoint. Included are hydrocarbons, alcohols, aldehydes, ketones, acids (aliphatic and carbocyclic) carbohydrates, phenols, proteins, peptides, amines, alkaloids, some nitro compounds, hormones, and vitamins. The last 180 pages are devoted to the determination of color in various technically important liquids.

Physical chemists who in their research need methods for the determination of traces of organic compounds (in photochemistry, in studies of inhibition, etc.) will find the book very helpful. In general, a complete review of the literature is given, followed by the sampling, the procedure, and the selection of proper standards. The compilation given is a valuable addition to the literature on the colorimetry of organic compounds, for which the authors deserve the recognition not only of organic and analytical chemists, but also of workers in the biological and medical fields.

I. M. KOLTHOFF.

THE HYDRATION AND PHYSICOCHEMICAL PROPERTIES OF PECTIN AND ITS DERIVATIVES

REINHOLD F. STUEWER

Department of Chemistry, Stanford University, California

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Although the properties and structure of pectin have been under investigation for many years, no agreement as to the complete structure has yet been reached. It is, however, usually conceded that a polygalacturonic acid is contained in the pectin molecule. According to Ehrlich (2), four galacturonic acid molecules, two of which are methylated, constitute the fundamental unit. Other views are those of Nanji, Paton, and Ling (8), who look upon pectin as having a ring structure containing four methylated galacturonic acid molecules and one each of galactose and arabinose. Morell, Baur, and Link (7) have concluded that at least eight or ten acid residues are contained in the pectic acid molecule. If the views of Nanji, Paton, and Ling be accepted, the normally acidic nature of pectin sols does not follow unless one assumes partial demethoxylation to have occurred in the preparation of the pectin. Spencer (11) explains this acid condition as being due to preferential adsorption of anions. However, since the methods used in preparation of pectins are such that demethoxylation takes place, it is permissible to assume that all pectins used in the making of jellies may be acidic of themselves.

While the degree of hydration of pectin is usually considered to be one of the factors involved in its jelling, no previous attempts to measure it directly have been made, although qualitative results have been reported (4). In this work, measurements of the hydration in alcohol suspensions were carried out.

It has long been known that the presence of salts is important in the jelling of pectin. Halliday and Bailey (6) showed that the effect of calcium chloride is such that the amount of sugar required to induce jelling is decreased. On the other hand, Spencer (11) finds that in the presence of acids sodium chloride decreases the jelling ability. It is generally agreed that the cation (4) is of more importance in these salt effects, although definite anion effects may be observed under proper conditions (5). Whereas some workers explain the behavior of pectin in the presence of salts as due to sorption effects only (11), others prefer the hypothesis that exchange of cations between the pectin molecule and the salt is involved

(5). Glückmann (5) has prepared and investigated the properties of pectins containing a number of anions in varying proportions.

In the present work an investigation has been made of the acidic character of pectin and of its hydration and sorption characteristics in the acidic and several salt forms.¹ An apple pectin was used. The acidic form was prepared by thoroughly washing the pectin with a 50 per cent alcohol solution containing hydrochloric acid. This treatment removed practically all of the metallic ions. The pectinic acid described is a product of low-temperature acid hydrolysis of pectin and the pectic acid a product of alkaline hydrolysis of pectin. The salt forms were prepared by the neutralization of the acid with the proper base in the presence of buffer salts containing the same cation. These buffer salts were then washed out by thorough extraction with 50 per cent alcohol. The combining weights of the three acids were found to be 848, 425, and 207, respectively, for vacuum-dried pectin, pectinic acid, and pectic acid.

EXPERIMENTAL

The conductance of pectic materials and their salts

Solutions of the materials were prepared by weighing out the proper amounts and dispersing them in conductivity water. Lower concentrations were prepared by dilution. The sodium salts used in these experiments were prepared by addition of the proper amount of sodium hydroxide to the acidic sol. The conductivities of acidic pectin and pectinic acid are given in table 1.

The conductivities of the sodium salts of the two materials are given in table 2.

The observed values of pH were obtained by means of a glass electrode. The calculated values were obtained by computation from the data of tables 1 and 2 and the ionic conductances of sodium and hydrogen. The calculation of the dissociation constant was made on the assumption that the same value obtains for all hydrogens, and, while not constant, it does give an indication of the acid strength of pectin and a pectinic acid. It is interesting to note that the values for the two materials are almost identical.

The conductances of the magnesium salts of the two materials and the calcium salt of the pectin were also determined. These values are given in table 3.

The data are of interest in that dissociation is far from complete even at extremely low concentrations, and may probably be looked upon as explaining, at least in part, the differences noted in the past in the effects of the various cations on the jelling of pectin.

¹ For nomenclature see A. W. Thomas: Colloid Chemistry, p. 371, McGraw-Hill Book Co., New York (1934).

TABLE 1
Conductivities of acidic pectin and pectinic acid

SUBSTANCE	NORMALITY	EQUIVALENT CONDUCTIVITY	pH		DISSOCIA- TION CONSTANT $\times 10^4$
			Calcu- lated	Ob- served	
Pectin	0.00825	64.1	2.87	2.85	2.9
	0.00330	89.3	3.13	3.10	2.3
	0.00132	118.7	3.43	3.38	1.9
	0.000528	138.8		3.71	1.2
	0.0001056	177.8	4.79	4.31	0.45
Pectinic acid.....	0.00941	61.7	2.81	2.81	2.9
	0.00376	83.9	3.10	3.08	2.4
	0.001505	105.0	3.40	3.38	2.0
	0.000602	123.3	3.60	3.71	0.94
	0.0001204	154.4	4.30	4.30	0.34

TABLE 2
Conductivities of sodium pectin and sodium pectinate

	EQUIVALENT CONDUCTIVITY	
	Sodium pectin	Sodium pectinate
0.0100	59.9	62.2
0.0040	65.1	67.1
0.0016	69.2	70.9
0.00064	72.8	75.3
0.000128	82.1	
0.000256		77.5
0.000041		78.0
0.0000256	73.7	

TABLE 3
Conductances of magnesium pectin, magnesium pectinate, and calcium pectin

NORMALITY	MAGNESIUM PECTIN		MAGNESIUM PECTINATE		CALCIUM PECTIN	
	Conductivity	Per cent dissociation	Conductivity	Per cent dissociation	Conductivity	Per cent dissociation
0.0100	38.4	49	29.1	36	36.7	43
0.0020	46.1	59	33.3	42	45.7	54
0.0004	52.4	67	39.2	49	51.4	60
0.00008	60.5	77	42.2	53	56.9	67

The conclusions from conductivity data were further substantiated by precision measurements² of the lowering of freezing point made by the

² All these measurements were made by Dr. Kurt H. Andresen, to whom my best thanks are due.

method of Scatchard (10), and, for the less dilute solutions, by measurements² of the lowering of vapor pressure made by the method of Robinson and Sinclair (9). The results were as given in table 4, where g (the osmotic coefficient) = $1 - j = \theta/v\lambda m$, where v is taken for the purpose of this calculation as 2 for sodium pectinate and as 3 for magnesium pectinate. It will be noted that the results from conductivity and the osmotic data are in close agreement.

Hydration of pectic materials

Experiments with the ultrafiltration method with methyl alcohol and also with sodium chloride as reference substance showed that pectin is hydrated to the extent of only about one-third of its weight of water. The experiments here described were made as follows, without ultrafiltration. Thoroughly dried materials were immersed in alcohol solutions of

TABLE 4
Osmotic coefficient of sodium pectinate and magnesium pectinate solutions

SODIUM PECTINATE SOLUTIONS		MAGNESIUM PECTINATE SOLUTIONS	
Normality	Osmotic coefficient g	Normality	Osmotic coefficient g
0.00088	0.9699	0.00417	0.4318
0.00163	0.9281	0.00630	0.3902
0.00241	0.8901		
0.00318	0.8572	0.00981	0.3233*
0.00392	0.8273	0.01209	0.3267*
0.0108	0.7683*		

* By lowering of vapor pressure; all others by freezing point.

known concentration and left in contact for about twenty-four hours. Samples of the supernatant liquid were then withdrawn and analyzed for alcohol content. This analysis was made by carefully distilling and then determining the alcohol content by means of a dipping refractometer. In cases where the concentration of the alcohol used was less than 20 per cent, an interferometer was used in analysis. Table 5 gives the data thus obtained. Hydrations are given in per cent of the dry weight of the material.

The form of the curves in figure 1 indicates that extrapolation to zero alcohol concentration is justified. Such extrapolation leads to the following values for the various materials in pure aqueous solution:

Pectin.....	25 per cent hydration
Pectic acid.....	21 per cent hydration
Sodium pectate.....	38 per cent hydration
Calcium pectate.....	35 per cent hydration

The tendency for pectin to disperse in solutions of alcohol of low concentration prevents their use with pectin and its salts; however, the simi-

TABLE 5
Hydration of pectic materials

SUBSTANCE	WEIGHT OF SOLUTION PER GRAM OF MATERIAL	INITIAL ALCOHOL CONCENTRATION	FINAL ALCOHOL CONCENTRATION	PER CENT HYDRATION
Acidic pectin.....	11.58	19.51	19.81	18.3
	12.20	32.77	34.42	23.1
	18.39	41.13	42.07	18.8
	9.81	49.86	51.12	24.8
	12.03	56.77	58.08	25.4
	6.42	60.15	62.42	23.3
	5.55	70.10	72.33	17.1
	5.23	80.43	82.35	12.3
	6.9	95.22	92.52	2.1
Pectic acid.....	10.0	95.09	96.41	6.8
	10.0	76.61	79.33	17.1
	10.0	71.66	74.47	18.9
	10.0	51.56	52.47	17.0
	10.0	42.14	43.78	19.0
	20.3	23.31	24.31	20.9
	10.0	10.77	11.33	20.3
	15.0	4.939	5.141	21.0
	14.4	1.162	1.206	21.2
Sodium pectate.....	10.0	76.61	80.03	21.4
	20.0	41.79	43.29	35.0
	21.0	32.52	33.66	35.0
	10.0	23.31	25.14	36.4
Calcium pectate.....	10.0	95.09	96.26	5.9
	10.0	76.61	80.03	21.4
	10.0	71.66	74.91	22.6
	10.0	51.94	54.76	25.7
	10.0	41.79	44.38	29.1
	10.1	41.79	44.14	26.7
	10.0	23.31	24.06	32.6
	10.0	10.77	11.50	32.7
	10.2	4.939	5.375	34.0
	10.2	1.162	1.273	37.0
Magnesium pectate.....	10.0	20.58	22.12	37.1

larity in the behavior of pectates and salts of pectin at high concentrations justifies the assumption that the same would hold true throughout. An experiment with 0.1 *N* hydrochloric acid in 40 per cent alcohol gave the

same hydration value for hydration of acidic pectin as the control in which water was used.

Table 6 summarizes the data for a number of materials. In this case all hydration values are for approximately 50 per cent alcohol, and so do not represent the hydrations at zero concentration of the reference substance.

In general the pectates appear to be slightly less hydrated than the salts of pectin or of pectinic acid. Also, the acids are in all cases definitely less hydrated than are the salts, and the calcium salts are less hydrated than either the sodium or the magnesium salts, the latter being hydrated to the

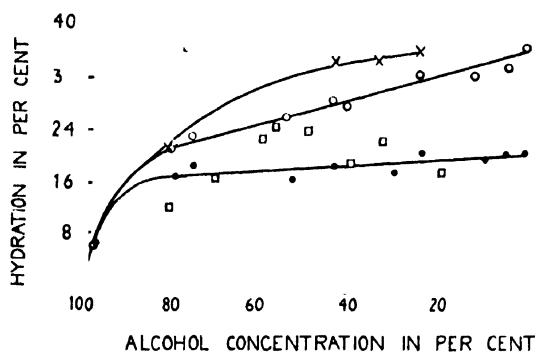


FIG. 1. Hydration of pectin and its derivatives. □, pectin; ●, pectic acid; ×, sodium pectate; ○, calcium pectate.

TABLE 6
Hydration of the acids and their salts in 50 per cent alcohol

	PER CENT HYDRATION OF			
	Acid	Sodium salt	Magnesium salt	Calcium salt
Pectin.....	25	33	33	
Pectinic acid.....	26	34	37	30
Pectic acid.....	19	33	33	27

same extent within the limits of error. One may conclude then that the degree of hydration in a pectin jelly will be dependent upon pH and upon the other cations present in the jelly. The degree of hydration appears to be dependent upon the degree of hydration of the cation and may also be correlated roughly with the degree of dissociation of the salt as previously described.

Sorption of potassium iodate by pectic materials

Sorption experiments were carried out by addition of dried materials to solutions of iodates, both in water and in alcohol solutions. Analyses of

the supernatant liquid were then made to determine the amount of sorption which had taken place. Necessarily, conditions used were at all times such that dispersion of the material did not take place to any appreciable extent. The nature of these materials under such conditions of non-dispersion must be similar to that of permutites. They are, therefore, subject to so-called exchange adsorption, which is merely the exchange of cations between the salt present and the colloidal material. Molecular sorption may also take place, and it is this type of sorption with which the following experiments are concerned. Specifically, the effect of various cations in both the sorbent and sorbate was investigated.

TABLE 7

Relative sorptive powers of pectic materials for potassium iodate

SUBSTANCE	SOLUTION USED								
	30 per cent alcohol			1.0 N sodium chloride			Water		
	Normality of KIO ₃								
	0.04	0.01	0.0025	0.2	0.02	0.002	0.2	0.01	0.002
Pectic acid	32.6	18.9	25.7	8.8	16.1	52.9		3.2	20.6
Magnesium pectate	29.1	28.7	30.6	1.2	5.2	19.8	2.0	4.6	15.9
Sodium pectate	3.9	1.3	0.6	-0.6	3.2	8.6			

TABLE 8

Per cent sorption of iodates by pectates

	0.04 N IODATE	0.01 N IODATE	0.0025 N IODATE
Potassium . .	2.4	0.4	2.0
Sodium	3.9	1.0	1.3
Magnesium . .	35.8	31.5	33.8
Hydrogen . . .	9.1	8.4	8.6

The data in table 7 were obtained by keeping the materials in contact with the solutions for eleven days with constant shaking. In all cases 14 g. of solution per gram of pectin was used. The iodate concentrations given are initial concentrations, and sorptive powers are expressed as the percentage of the iodate sorbed, without allowance for hydration.

A similar series of experiments was run in which each pectic material was allowed to remain in contact with the corresponding iodate in 30 per cent alcohol solution for a week with constant shaking. The results were as given in table 8.

It is apparent from the data in tables 7 and 8 that the effects of the ions on adsorption of iodate are quite marked. The potassium and sodium salts do not sorb nearly as much of the potassium iodate as do the acid and

the magnesium salt. The sorption is much greater from sodium chloride than from water solution when pectic acid is the sorbent, but it is not much different when magnesium pectate is used. This at first sight appears to be in disagreement with the fact that hydrogen ions and magnesium ions are about equally effective in sorption from alcohol solution, but it is explainable on the basis of greater displacement of magnesium than of hydrogen from the pectic molecule by the relatively ineffective sodium ion. Actually such a difference exists even in the sorption from alcohol solution, and the magnesium ion is considerably more effective in promoting sorption than is the hydrogen ion, as shown by table 8, where sorbent and sor-

TABLE 9

The effect of total electrolyte concentration on the progress of adsorption

PER CENT SORPTION FROM WATER SOLUTIONS			PER CENT SORPTION FROM 1.0 N SODIUM CHLORIDE		
Initial KIO ₃	Final KIO ₃	Sorption	Initial KIO ₃	Final KIO ₃	Sorption
<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>
0.0687	0.0685		0.0591	0.0481	18.6
0.137	0.140		0.261	0.234	10.4
0.279	0.283		1.044	0.960	8.1
0.591	0.588		4.427	4.103	7.3
1.208	1.183	2.1			
1.991	1.922	3.5			
4.485	4.278	4.6			

TABLE 10

Rate of sorption of potassium iodate on magnesium pectate

	WATER SOLUTIONS				1.0 N SODIUM CHLORIDE SOLUTIONS			
	0	10 min.	4 hr.	24 hr.	0	10 min.	4 hr.	24 hr.
Time.....								
Per cent KIO ₃	0.0409	0.0426	0.0419	0.0405	0.0381	0.0377	0.0374	0.0364
Per cent sorbed....		-3.5	-2.4	1.0		1.1	1.8	4.4

bate contain the same cation. That the exchange of magnesium and sodium does not take place to a very great extent, however, follows from the fact that magnesium pectate is insoluble in water. The greater acid strength of iodic acid than of pectic acid precludes any very great exchange of potassium and hydrogen in the case of potassium iodate and pectic acid.

The effect of total electrolyte concentration on the progress of adsorption is shown in the data in table 9, which were obtained in experiments in which overnight contact between solution and sorbent was allowed.

The marked difference at low concentrations is certainly to be attributed to electrical effects, and in the above data is due both to a difference in the manner in which sorption progresses and to the lack of equilibrium

at the low concentrations. It can be shown that in the presence of small electrolyte concentrations an initial negative sorption takes place, which later becomes positive in many cases, whereas in the presence of a greater amount of electrolyte to suppress the Donnan effect, the sorption is at once positive. The data in table 10 serve to illustrate this point.

Sorption is greater at high than at low concentrations in the case of sodium pectate sorbing iodate from alcohol solutions (see table 7). In general, the sorption from alcohol solutions is abnormal in that it does not follow the adsorption isotherm, and the per cent sorption may be greater at high than at low concentrations.

Since pectin itself is readily dispersible, an extensive comparison of its sorptive properties with those of pectic acid could not be carried out; however, a comparison of sorption from alcohol solutions was made.

TABLE 11
Sorption of potassium iodate from 40 per cent alcohol solution

SORBENT	PER CENT OF IODAT	
	Initial KIO ₃ concentration 0.487 per cent; 3 days shaking	Initial KIO ₃ concentration 0.058 per cent; 7 days shaking
Pectin.....	45.2	19.0
Pectinic acid.....	29.7	28.7
Pectic acid.....	32.7	15.6
Sodium pectin.....	Dispersed	Dispersed
Sodium pectinate.....	10.9	10.5
Sodium pectate.....	9.2	3.1
Magnesium pectin.....	25.9	27.0
Magnesium pectinate.....	37.3	39.6
Magnesium pectate.....	47.2	45.6

One may conclude that qualitatively the same effects of cations are to be found with pectin and pectinic acid and their salts as with pectic acid. Insufficient data are obtainable to determine the quantitative relationships precisely, but the data do show that the effects vary in magnitude with the various materials under the conditions of this experiment.

GENERAL DISCUSSION

The conductivity data reported substantiate the views held by those who consider pectin to be acidic of itself, and are in agreement with the facts as regards the effect of acidity in pectin jellies. These data show pectin to be a weak acid, but very definitely stronger than acetic acid. The contention of Glückmann to the effect that the acidic pectin is freed

from its salts in pectin jellies is justified, although in practice jellies are not always of sufficiently low pH to cause complete conversion. The fact that the sodium salt is highly dissociated, the salts of divalent metals are considerably less dissociated, and the acid still less is in agreement with the reported facts (11, 6, 3) that sodium salts hinder jelling while calcium chloride promotes it and that acids are particularly effective in causing jelling in the presence of an organic substance such as sucrose.

The data on hydration show that, as Spencer postulates, the addition of acid to pectin decreases the hydration, since the acidic pectin set free is less hydrated than the salt. On the other hand, the postulate that the effect of sugar is one of dehydration of the pectin micelles does not appear to follow, for although a very slight change in hydration occurs with change in alcohol concentration, the great differences which may be obtained in jelling ability with small changes in concentration of the organic precipitant seem not to be accounted for by dehydration.

That sorption effects are of only minor importance seems to be indicated by the fact that the effect of acidity is mostly one of pH (12). Differences due to the anion present in the acid have been observed (5, 1). A further indication is the fact that, according to the data here presented, sorption is most marked when hydrogen or a divalent metal is present in the pectin molecule, and almost negligible in the case of monovalent metals. Yet anion adsorption should tend to stabilize the pectin, and so this stabilizing effect is greatest, but still overshadowed, in the presence of cations which promote jelling.

In short, pectin is a self-stabilized colloid, its charge resulting from the ionization of the pectic molecule itself. In the form of its highly ionized sodium salt, the charge is great and the stability is accordingly greater than in the case of the less ionized calcium salt. In the acid the ionization is still less and consequently the charge is smaller. An added stabilizing effect is that due to sorption of anions, but this effect appears to be a minor one under ordinary conditions. Its magnitude is dependent upon the anion itself and upon the cations present. The degree of hydration is in the same order as the degree of dissociation in the case of the acid and the calcium and sodium salts; however, the magnesium salt is less dissociated but just as highly hydrated as the sodium salt. The main differences between salts of monovalent and divalent metals are due to unequal dissociation, and differences between salts of ions of the same valence are probably attributable to differences in hydration which affect stability.

SUMMARY

The hydration of pectin and of a number of its derivatives has been measured by the method of a reference substance in water and in aqueous alcohol, in agreement with results by ultrafiltration. It is found that the

hydrate water amounts to 0.25, 0.21, 0.38, and 0.35 g. of water to 1 g. of pectin, pectic acid, sodium pectate, and calcium pectate, respectively. That of pectinic acid resembles pectin; the three sodium and the three magnesium derivatives are somewhat more hydrated.

The sorption of potassium iodate by these materials has been studied.

Pectin and pectinic acid are weak acids, definitely stronger than acetic acid. The sodium salts are moderately strong electrolytes, but the magnesium and calcium salts are far from completely dissociated, even in $N/10,000$ solution.

Conclusions are drawn as to the colloid nature of pectin and its derivatives.

Our sincere thanks are due to Professor James W. McBain, under whose supervision this work was carried out.

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THE FREE ENERGY OF FORMATION OF ETHYL PROPIONATE EQUILIBRIUM IN THE GASEOUS STATE¹

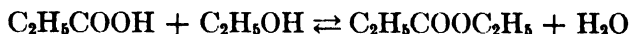
HARRY ESSEX AND MARJORIE SANDHOLZER

Department of Chemistry, Syracuse University, Syracuse, New York

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INTRODUCTION

In this investigation a determination of the standard free energy of formation of ethyl propionate has been made, using the method employed by Essex and Clark (2) for the determination of the standard free energy of formation of ethyl acetate. The standard free energy change of the reaction



has been calculated at several temperatures from carefully determined values of the equilibrium constant of the reaction in the gaseous state, which, together with data already available in the literature, leads to an evaluation of the standard free energy of formation of ethyl propionate. Silica gel was the catalyst used for this esterification reaction.

EXPERIMENTAL

A. Preparation of pure reagents

Commercial ethyl alcohol was purified by the same process used by Essex and Clark (2), and only that fraction distilling over within 0.1°C. was accepted for use in this investigation. This fraction was distilled directly into a bottle containing twice-distilled water, thus giving a dilution of alcohol which could be kept in a state of constant composition more easily than the undiluted alcohol. Its specific gravity at 20°C. compared to water at 4°C. was 0.81006, corresponding to 92.916 per cent alcohol.

The propionic acid used was a "c.p." product from the Eastman Kodak Company, and was further purified by fractionation. The fraction used had a boiling point range of 141.1°C.-141.5°C., and a specific gravity of 0.99534 at 20°C. compared to water at 4°C. It was standardized by titra-

¹ Submitted by Marjorie Sandholzer to the Faculty of Syracuse University in partial fulfillment of the requirements for the degree of Doctor of Philosophy, May, 1936.

tion with the standard barium hydroxide solution which gave a value of 99.88 per cent propionic acid.

The ethyl propionate was also a "C.P." product from the Eastman Kodak Company and was further purified by fractionation. The fraction used had a boiling point range of 98.9°C.-99.3°C., and a specific gravity of 0.8907 at 20°C. compared to water at 4°C. It was standardized by hydrolysis with the standard barium hydroxide solution, which gave a value of 99.72 per cent ethyl propionate.

Barium hydroxide was used to follow the progress of the esterification reaction. It was standardized by weight titration, first against succinic acid, and finally against a sample of pure benzoic acid from the Bureau of Standards.

Twice-distilled water was used in the experimental work.

The silica gel used was the commercial product from the Silica Gel Corporation of Baltimore, Maryland.

B. Apparatus and procedure

The apparatus was that used by Essex and Clark (2), with the exception of an improved automatic temperature control consisting of a mercury regulator which kept the temperature constant to within 0.4°C. maximum difference.

Equilibrium was determined by the same dynamic method used by Essex and Clark, and the equilibrium product was analyzed by the same method of weight titration against standard barium hydroxide solution.

C. Preliminary experiments

Preliminary experiments were run to determine the stability of the system relative to heat, and the approximate equilibrium position. A small test apparatus was set up and mixtures of the reactants were passed over the catalyst at several temperatures. The absence of uncondensed gases in the product and a negative test for aldehydes were accepted as sufficient evidence of the absence of decomposition reactions. There were no uncondensed gases produced up to a temperature of 225°C. The ammoniacal silver oxide test for aldehydes was applied both to the pure reagents and to the condensates from the final runs. In no case was an appreciable amount of aldehyde shown.

It became evident from the preliminary experiments that the equilibrium mixture produced by the action of 1 mole of acid on 1 mole of alcohol is not miscible, since the condensate formed two liquid layers. With initial mixtures sufficiently rich in water, however, homogeneous equilibrium mixtures are obtained. The equilibrium mixtures must be homogeneous as in the final and accurate runs, initial mixtures approximating the equilibrium mixtures must be used, and these initial mixtures must,

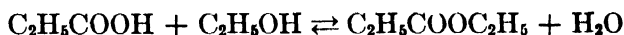
evidently, be homogeneous. The mixture which proved most satisfactory was that which would be produced at equilibrium by the action of 100 moles of water upon 1 mole of ester.

Some preliminary tests were carried out to determine the error involved in titrating propionic acid in the presence of ethyl propionate. Duplicate samples of the acid were titrated with barium hydroxide, using phenolphthalein as the indicator, with and without the addition of ethyl propionate. No appreciable error was found in titrating the acid in the presence of the ester, provided an excess of the base was avoided and care was exercised in recognizing the first permanent end point.

Before the final runs were made, the reaction vessel and catalyst were thoroughly cleaned by treatment with oxygen as described by Essex and Clark (2).

THE EQUILIBRIUM MEASUREMENTS

The equilibrium was determined at three temperatures, namely, 155°C., 170°C., and 200°C. At each temperature, after an approximate determination of the equilibrium position by preliminary experiments, carefully controlled runs were made with (a) a reaction mixture richer in acid and alcohol than the equilibrium mixture, (b) a reaction mixture richer in ester and water than the equilibrium mixture, and (c) a reaction mixture having exactly the equilibrium concentrations as calculated from the average composition of the products of the runs (a) and (b). A single run, richer in ester and water than the equilibrium mixture, was made at the additional temperature of 184.7°C. Each reaction mixture was made up in proportions which would be reached at some stage in the reaction



if the initial mixture contained ester and water alone in the proportion of 100 moles of water to 1 mole of ester. Since the proportions of the acid, alcohol, and ester compared to the water in the reaction mixtures were always small, and since they are quite volatile, it did not seem accurate enough to make up the mixtures by weighing out the required amount of each constituent into an open container (the method used by Essex and Clark). Therefore the required amount of each of these volatile constituents was weighed out in a tared glass bulb drawn down to a capillary and thus readily sealed off after the sample had been introduced. These bulbs were filled by immersing them in a bottle of the liquid and reducing the pressure on the surface by means of a suction pump. The air contained in the bulb bubbled out and when the pressure on the surface of the liquid was again increased, the liquid was forced into the bulb. This process was repeated until the bulb was filled as completely as desired. These sealed bulbs containing the acid, alcohol, and ester were placed in a

TABLE 1

Results of experiments

Reaction mixture ratios: C_2H_5COOH , 0.707 mole; C_2H_5OH , 0.707 mole;
 $C_2H_5COOC_2H_5$, 0.293 mole; H_2O , 99.293 moles. Temperature, $155^\circ C$.

Weight per cent of acid in the reaction mixture, 2.75

DURATION OF RUN	WEIGHT OF PRODUCT COLLECTED	WEIGHT OF BASE (AQ.) REQUIRED TO NEUTRALIZE PRODUCT	WEIGHT PER CENT OF ACID IN PRODUCT
<i>minutes</i>	<i>grams</i>	<i>grams</i>	
45	7.3573	8.9121	3.113
50	11.3196	13.7994	3.133
70	7.9887	9.6797	3.114
35	8.4006	10.1685	3.111
35	7.5830	9.2675	3.141
60	9.3314	11.4210	3.146
45	11.9357	14.4266	3.106
45	11.2228	13.5442	3.102
60	8.0933	9.7627	3.100
90	9.4104	11.4498	3.127
45	8.4683	10.4224	3.163
65	14.6363	17.7385	3.115
Average			3.123

$$K_a \left(K_a = \frac{a_{\text{(ester)}} a_{\text{(water)}}}{a_{\text{(acid)}} a_{\text{(alcohol)}}} \right) \text{ for average} = 30.67$$

TABLE 2

Summary of results

TEMPERATURE	WEIGHT PER CENT OF ACID IN REACTION MIXTURE	AVERAGE WEIGHT OF ACID IN PRODUCT	K_a
$^\circ C$.			
155	2.75	3.123	30.67
	3.11	3.133	30.09
	3.60	3.104	31.80
170	2.75	3.205	25.90
	3.21	3.187	26.89
	3.21	3.190	26.71
	3.60	3.209	25.67
184.7	3.21	3.260	22.96
200	3.21	3.322	19.90
	3.32	3.313	20.32
	3.60	3.324	19.78

glass-stoppered bottle into which had already been weighed the required amount of water. Since the bulbs were blown of very thin glass, a vigorous shaking of the bottle was sufficient to shatter them and produce a complete mixture of the reaction constituents.

Runs were made over a considerable range of rates of flow with each reaction mixture at each temperature. The results of the run at 155°C. from the ester-rich side are presented in detail in table 1. Independence of the per cent of acid in the product on the rate of flow is further evidence of the absence of side or consecutive reactions. The results of the runs at all four of the temperatures used are summarized in table 2.

The probable error in the determination of the per cent of acid at each temperature was calculated by the method of least squares, using at each temperature all the determined values of acid percentages in the products after constancy in composition was attained. Each run consisted of a considerable number of these determined values of acid percentages, as shown in table 1.

TABLE 3
Summary of the equilibrium determinations

TEMPERATURE °C.	PER CENT OF ACID IN PRODUCTS	PROBABLE ERROR IN DATA OF COLUMN 2	AVERAGE VALUES OF K_a
155	3.122	0.00269	30.85
170	3.200	0.00279	26.29
184.7	3.260	0.00452	22.96
200	3.320	0.00151	20.00

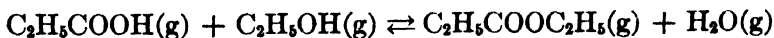
The results of all the equilibrium determinations have been summarized in table 3.

CALCULATIONS

A. Molal composition of the equilibrium mixture

1. The number of moles of each constituent

At the temperatures at which measurements were made, no products were detected other than those entering into the reaction



The molal composition of the gaseous mixture leaving the reaction tube was calculated from the composition of the entering mixture and the acid in the product.

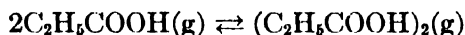
For example, in one experiment at 155°C., the mixture entering the reaction tube contained 2.75 per cent of propionic acid, corresponding to the following number of formula weights of each constituent per 100 g.

of the mixture: acid, 0.03714; alcohol, 0.03714; ester, 0.01539; water, 5.216.

This mixture was passed over the heated catalyst. The final product, after constancy in the acid percentage had been reached, analyzed 3.123 per cent propionic acid. This shows a shift of the equilibrium in the direction of acid and alcohol formation, and corresponds to an increase of 0.005037 formula weights of acid and of alcohol per 100 g., and a like decrease in the number of formula weights of ester and water. Therefore, in this final product there were 0.04218 formula weights of acid and alcohol, 0.01035 formula weight of ester, and 5.211 formula weights of water. For alcohol, ester, and water, the formula weights are the number of moles; these are listed in table 6 in the columns headed n_3 , n_4 , and n_5 , respectively.

The work of Miss Klein (8) on the association and fugacity of gaseous propionic acid indicates that even at a temperature of 184°C. and a pressure of 140 mm. propionic acid exists partly as double molecules. At lower temperatures even greater complexity is shown.

The association constant of the reaction



is given by the relation

$$K_x = \frac{P_{(\text{C}_2\text{H}_5\text{COOH})_2}}{P_{\text{C}_2\text{H}_5\text{COOH}}^2} \quad (1)$$

where $P_{(\text{C}_2\text{H}_5\text{COOH})_2}$ is the partial pressure of the double molecules of propionic acid, and $P_{\text{C}_2\text{H}_5\text{COOH}}$ is the partial pressure of the single molecules.

The number of moles of $\text{C}_2\text{H}_5\text{COOH}$ (n_1), and of $(\text{C}_2\text{H}_5\text{COOH})_2$ (n_2) per 100 g. of our reaction product may be calculated from this K_x and the number of moles of alcohol (n_3), of ethyl propionate (n_4), of water (n_5), and the number of formula weights of propionic acid (w). The partial pressures of $(\text{C}_2\text{H}_5\text{COOH})_2$ and $\text{C}_2\text{H}_5\text{COOH}$ in our products are given respectively by the equations

$$P_{(\text{C}_2\text{H}_5\text{COOH})_2} = \frac{n_2}{n_1 + n_2 + n_3 + n_4 + n_5} \times 1 \quad (2)$$

and

$$P_{\text{C}_2\text{H}_5\text{COOH}} = \frac{n_1}{n_1 + n_2 + n_3 + n_4 + n_5} \times 1 \quad (3)$$

1 being the total pressure in atmospheres of these experiments. That is, each partial pressure is the product of the mole fraction and the total pressure. Substituting these values into equation 1,

$$K_x = \frac{n_2(n_1 + n_2 + n_3 + n_4 + n_5)}{n_1^2} \quad (4)$$

If G is the grams of propionic acid in the equilibrium products, then

$$G = 74.05n_1 + 148.10n_2$$

and

$$w = \frac{G}{74.05} = n_1 + 2n_2$$

or

$$n_2 = \frac{w - n_1}{2} \quad (5)$$

Upon substituting the value of n_2 (equation 5) into equation 4

$$K_x = \frac{\frac{w - n_1}{2} \cdot \left(n_1 + \frac{w - n_1}{2} + n_3 + n_4 + n_5 \right)}{n_1^2}$$

from which

$$n_1 = \pm \sqrt{\frac{2w}{4K_x + 1} \left(\frac{w}{2} + n_3 + n_4 + n_5 \right) + \left(\frac{n_3 + n_4 + n_5}{4K_x + 1} \right)^2} - \frac{n_3 + n_4 + n_5}{4K_x + 1} \quad (6)$$

In order that n_1 be positive, the sign preceding the square root must be positive. This expression (equation 6) may be used to find the number of single moles of propionic acid (n_1) in the equilibrium mixture from its percentage composition. The number of double moles of propionic acid (n_2) may be obtained by substituting the numerical value of n_1 into equation 5.

2. Evaluation of K_x at the temperatures of the experiments

The K_x values of table 4 were taken from the work of Miss Klein (8). From these values, K_x is given as a function of temperature by the relation (throughout this paper, $\ln = \log_e$, while $\log = \log_{10}$)

$$\log K_x = \frac{5615.87}{T} + 14.1416 \log T - 50.47295 \quad (7)$$

Substituting for T the desired temperature and solving for K_x , the results of table 5 were computed.

The values of K_x , n_1 (calculated from equation 6), n_2 (calculated from equation 5), n_3 , n_4 , and n_5 are listed in table 6.

B. Activities of the constituents of the mixture at equilibrium

For the esterification reaction under consideration the activity equilibrium constant K_a is

$$K_a = \frac{a_4 \times a_5}{a_1 \times a_3} \quad (8)$$

in which a_1 , a_3 , etc., are the activities of the acid, alcohol, ester, and water, respectively, in the equilibrium mixture.

At the low total pressure of these experiments, namely 1 atm., and the low partial pressures of the several constituents of the resulting mixture at equilibrium, it is justifiable to substitute for the activities of the alcohol,

TABLE 4

Values of K_x at the three different temperatures

T ..	372.1°	412.1°	457.1°
K_x .	9.390	1.364	0.269

TABLE 5

Values of K_x at the temperatures of the experiments

T	428.1°	443.1°	457.8°	473.1°
K_x	0.7236	0.4235	0.2633	0.1681

TABLE 6

Composition of the equilibrium mixtures in moles

T IN °K.	K_x	w	n_1	n_2	n_3	n_4	n_5
428.1	0.7236	0.04218	0.04170	0.000237	0.04218	0.01035	5.211
		0.04192	0.04146	0.000234	0.04192	0.01061	5.211
		0.04231	0.04184	0.000239	0.04230	0.01022	5.211
443.1	0.4235	0.04334	0.04306	0.000140	0.04334	0.00919	5.210
		0.04328	0.04299	0.000145	0.04328	0.00925	5.210
		0.04304	0.04275	0.000145	0.04303	0.00949	5.210
		0.04308	0.04279	0.000145	0.04307	0.00945	5.210
457.8	0.2633	0.04402	0.04383	0.000095	0.04402	0.00850	5.209
473.1	0.1681	0.04486	0.04474	0.000060	0.04486	0.00767	5.208
		0.04489	0.04476	0.000065	0.04489	0.00764	5.208
		0.04474	0.04461	0.000065	0.04475	0.00779	5.208

ester, and water in the gaseous mixture their mole fractions, and equation 8 becomes

$$K_a = \frac{N_4 \times N_5}{a_1 \times N_3} \quad (9)$$

The results of several investigators support this assumption. The experimental data used by Gibson and Sosnick (5) for mixtures of ethylene and argon indicate practical identity of fugacity and mole fraction at 1 atm. pressure, and the assumption is further justified by the experimental

results obtained by Lurie and Gillespie (11) for mixtures of ammonia and nitrogen. Of more particular application, moreover, are the results of Essex and Kelly (3) for mixtures of alcohol and water which well support such an assumption. These mole fractions are

$$N_3 = \frac{n_3}{n_1 + n_2 + n_3 + n_4 + n_5}$$

$$N_4 = \frac{n_4}{n_1 + n_2 + n_3 + n_4 + n_5} \quad \text{etc.}$$

Since the gas mixture is justifiably assumed to be very nearly ideal, the partial pressure due to single molecules of propionic acid may be substituted for its fugacity or activity. This partial pressure or fugacity of the propionic acid in the equilibrium mixture may be calculated from the following relation,

$$P_1 = f = \frac{\sqrt{1 + 4KP} - 1}{2K} \quad (10)$$

In this equation K is the quantity previously indicated by K_x . The fugacity of the propionic acid gas may be calculated by substituting for K the association constant of propionic acid at the temperature of the experiment, and for P the partial pressure of the propionic acid gas, which is equal to the sum of the partial pressures of the single and double molecules, and given by the expression,

$$P_{(\text{acid})} = \frac{n_1 + n_2}{n_1 + n_2 + n_3 + n_4 + n_5} \times 1 \quad (11)$$

The values of $P_{(\text{acid})}$ and K_x of table 7, when substituted into equation 10, give the values for the fugacity of propionic acid, $f_{(\text{acid})}$, listed in this same table.

*C. Equilibrium constant and standard free energy of the gaseous reaction.
Heat of gaseous reaction*

At any temperature, the standard free energy change, ΔF^0 , of a reaction is related to the activity equilibrium constant by the equation

$$\Delta F^0 = -RT \ln K_a \quad (12)$$

By substituting the numerical values of K_a and the corresponding temperatures, the values of ΔF^0 listed in table 7 were calculated. The maximum variation in the ΔF^0 values calculated from the different K_a values given at each temperature is 1.6 per cent.

Expressing ΔF^0 as a function of temperature by means of

$$\Delta F^0 = \Delta H_0 - \Delta G_0 T \ln T + IT \quad (13)$$

and solving three simultaneous equations involving the values of ΔF^0 from the experimentally determined equilibrium constants, the following equation was obtained

$$\Delta F^0 = -8381.03 - 10.0076T \ln T + 73.4090 T \quad (14)$$

From equation 14, $\Delta F^0_{298.1}$ equals -3497.8 cal., or K_a equals 365.3.

TABLE 7
Activity data and standard free energies of the gaseous reactions

T IN $^{\circ}\text{K.}$	K_x	$P_{(\text{acid})}$	$f_{(\text{acid})}$	N_2	N_4	N_6	K_a	AVERAGE K_a	ΔF^0 FROM K_a
428.1	0.7236	0.007905	0.007863	0.007950	0.001951	0.9822	30.65	30.85	-2919.2
		0.007859	0.007815	0.007902	0.002000	0.9822	31.81		
		0.007932	0.007884	0.007973	0.001926	0.9822	30.09		
443.1	0.4235	0.008142	0.008115	0.008169	0.001732	0.9820	25.66	26.29	-2880.5
		0.008130	0.008103	0.008157	0.001743	0.9820	25.90		
		0.008085	0.008058	0.008111	0.001789	0.9820	26.88		
		0.008093	0.008065	0.008118	0.001781	0.9820	26.71		
457.8	0.2633	0.008279	0.008260	0.008297	0.001603	0.9818	22.96	22.96	-2852.6
473.1	0.1681	0.008444	0.008432	0.008456	0.001445	0.9817	19.90	20.00	-2818.3
		0.008449	0.008440	0.008461	0.001440	0.9817	19.79		
		0.008421	0.008409	0.008436	0.001468	0.9817	20.32		

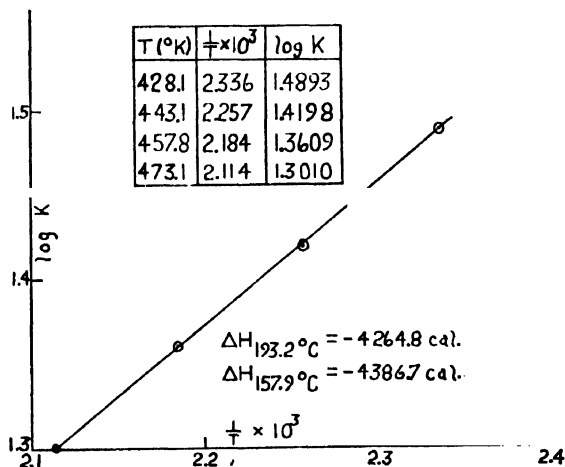


FIG. 1. Curve showing change of K_a with temperature

The heat of the reaction, ΔH , may be calculated by plotting $R \ln K_a$ against $1/T$. This has been done in the curve of figure 1. The individual points fall upon a curve which is very nearly a straight line, showing that the heat of the reaction is practically independent of the temperature.

The negative values of the slope of the curve (ΔH) at two different temperatures are listed.

Temperature, °C.....	193.2	157.9
ΔH in calories.....	-4264.8	-4386.8

On substituting the previously determined values of ΔH_0 and $\Delta \Gamma_0$ into the integrated form of Kirchoff's equation

$$\Delta H(298.1^\circ, g) = -5397.76 \text{ cal.}$$

*D. Standard free energy change on vaporization of the liquid constituents.
Heats of vaporization*

The vapor pressure data of table 8 are taken from the International Critical Tables (6). From each vapor pressure the standard free energy change on vaporization was calculated from the relation

$$\Delta F^0 = -RT \ln P$$

TABLE 8
Vapor pressure data

<i>T</i>	VAPOR PRESSURE FOR ALCOHOL	VAPOR PRESSURE FOR ETHYL PROPIONATE
°K.	mm.	mm.
293.1	43.9	27.75
303.1	78.8	47.75
313.1	135.3	77.9

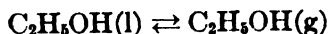
From the three values of ΔF^0 obtained in this manner for the vaporization of each liquid, the constants ΔH_0 , $\Delta \Gamma_0$, and I were found by solving three equations of the form

$$\Delta F^0 = \Delta H_0 - \Delta \Gamma_0 T \ln T + IT \quad (15)$$

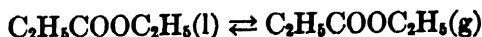
for the unknowns. The standard free energy change on vaporization at 298.1°K. was then calculated from equation 15, and the heat of vaporization at the same temperature was calculated from the constants ΔH_0 and $\Delta \Gamma_0$ and the equation

$$\Delta H = \Delta H_0 + \Delta \Gamma_0 T$$

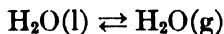
For alcohol, the values of the constants are: $\Delta H_0 = 14,359.88$; $\Delta \Gamma_0 = -13.5044$; and $I = -120.049$; and for the reaction



$\Delta F_{(298.1)}^0 = 1513.31 \text{ cal.}$ and $\Delta H_{(298.1)} = 10,334.22 \text{ cal.}$ For ethyl propionate the values of the constants are: $\Delta H_0 = 20,230.64$; $\Delta \Gamma_0 = -35.7028$; and $I = -265.288$; and for the reaction



$\Delta F_{(298.1)}^0 = 1796.93$ cal., and $\Delta H_{(298.1)} = 19,166.34$ cal. For the reaction



the standard free energy change and heat of vaporization were taken directly from the International Critical Tables and are: $\Delta F_{(298.1)}^0 = 2053$ cal. and $\Delta H_{(298.1)} = 10,450$ cal.

Saturated propionic acid vapor is highly associated at 298.1°K. Therefore its vapor pressure cannot be substituted for its activity nor can its fugacity be calculated by equation 10, which holds only for those conditions under which the gas consists only of single and double molecules. Essex and Clark used the following indirect method of arriving at the standard free energy change on vaporization of acetic acid at 298.1°K. First, the fugacity of the saturated vapor at each of three different temperatures for which data were available in the literature was calculated. This was done by determining the fugacity at some low pressure at each temperature by use of equation 10, and then calculating the fugacity at the saturation pressure from the relation

$$\log f_{P_2} = \frac{A}{2.303 RT} + \log f_{P_1} \quad (16)$$

in which f_{P_2} is the fugacity at the saturation pressure of the temperature T , f_{P_1} is the fugacity at the lower pressure (calculated by equation 10), and A is the area under the P - V curve from P_1 to P_2 . From the value of the fugacity of the saturated vapor, the standard free energy change on vaporization at each temperature was obtained from the relation

$$\Delta F^0 = -RT \ln f$$

From the ΔF^0 values at three different temperatures the constants in the relation

$$\Delta F^0 = \Delta H_0 - \Delta \Gamma_0 T \ln T + IT$$

were evaluated, and then it was solved for $T = 298.1^\circ\text{K}$.

The same procedure was followed in finding the standard free energy change on vaporization at 298.1°K. for propionic acid in this investigation. However, since the data available were inadequate for these calculations, it was necessary to extend them by some further experimental measurements. Miss Klein's (8) α - P curve $\left(\alpha = \frac{RT}{P} - V\right)$ for propionic acid at 99°C. covers a pressure range from 84 mm. to 135.2 mm., and that at 139°C. covers a range from 111.7 mm. to 525.3 mm. Using the method of Blackman (1), P - V measurements were made at each of these temperatures to extend these α - P curves up to the respective saturation pressures (173.4 mm. at 99°C., and 738.3 mm. at 139°C.). The 2.5 per cent to 3.0

per cent accuracy attained in these measurements was considered quite sufficient for the purpose of this calculation, since a slight error in the extension of the curve would make little difference in the total value of the area under the curve, which is itself a relatively small factor in equation 16. The α - P curve for a third temperature, 117°C., was also obtained by making experimental P - V measurements at the higher pressures up to the saturation pressure of 345.3 mm., and by calculating the molal volumes at the lower pressures from the relation

$$V = \frac{RT}{2P} + \frac{1}{2} \left(\frac{1}{4KP + 1} \right)^{\frac{1}{2}} \times \frac{RT}{P}$$

This relation should hold accurately at low pressures where only single and double molecules exist and where the gas laws hold accurately.

TABLE 9
Fugacities of propionic acid at saturation pressures

T	P_1	P_2	K_z	A	P_1	P_2
°K.	atm.	atm.		liter-atm.		
372.1	0.1779	0.2282	9.390	2.7537	0.0942	0.1104
390.1	0.1316	0.4543	3.685	9.4979	0.0969	0.2487
412.1	0.6579	0.9714	1.364	3.4346	0.4140	0.5523

From the α - P curve and the fugacity at some low pressure (calculated by equation 10) the fugacity at the saturation pressure was calculated at each of the three temperatures, 99°C., 117°C., and 139°C., by the relation

$$\ln f_2 - \ln f_1 = \ln P_2 - \ln P_1 - \frac{1}{RT} \int_{P_1}^{P_2} \alpha dP$$

where

$$\alpha = \frac{RT}{P} - V$$

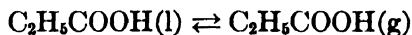
and V is the molal volume at the temperature T . The data and results of these calculations appear in table 9, where A is the area under the α - P curve from P_1 to P_2 , or the quantity

$$\int_{P_1}^{P_2} \alpha dP$$

By the procedure Essex and Clark used in their calculations on acetic acid, the following standard free energy changes on vaporization of propionic acid at the three different temperatures were obtained: $\Delta F_{372.1}^0 = 1630.8174$; $\Delta F_{390.1}^0 = 1079.4960$; and $\Delta F_{412.1}^0 = 486.5631$. From these the constants in the following equation were evaluated

$$\Delta F^0 = 40,691.434 + 72.5895T \ln T - 534.720T$$

from which, for the reaction

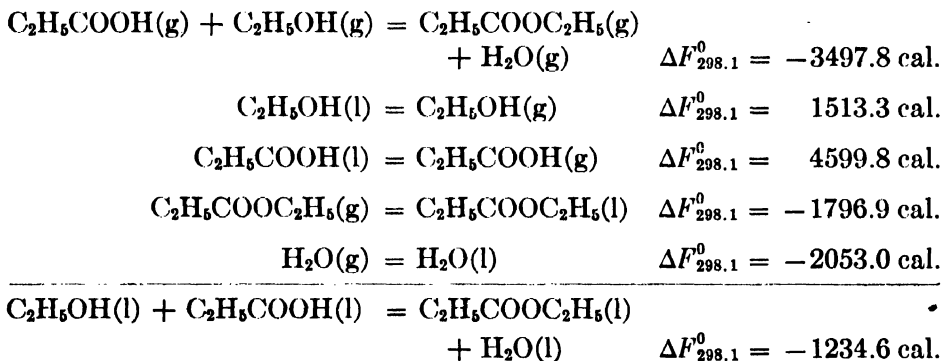


$$\Delta F_{298.1}^0 = 4599.79 \text{ cal. and } \Delta H_{298.1} = 19,052.50 \text{ cal.}$$

E. Standard free energy change of the liquid reaction. Free energy of formation of ethyl propionate

1. Standard free energy change of the liquid reaction

By combining algebraically the vaporization equation of each pure constituent and the esterification reaction in the gaseous state, the standard free energy change for the esterification reaction in the liquid state may be calculated.



or $K_{a(298.1, 1)} = 8.03$.

2. Free energy of formation of ethyl propionate

From heat capacity measurements at low temperatures, Parks and his coworkers (12) have computed, with the aid of the third law of thermodynamics, the standard free energy of formation of ethyl alcohol to be $-42,200$ cal. From the results of similar computations for several acids they suggest the equation

$$\Delta F_{298}^0 = -96,000 + 1080n$$

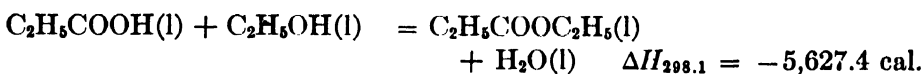
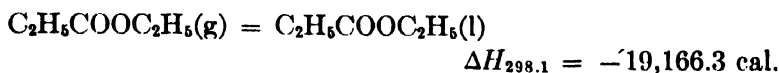
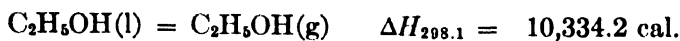
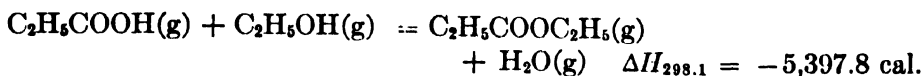
for obtaining the molal free energy of formation in the liquid state of a normal, saturated, aliphatic acid containing n carbon atoms. From this equation, $\Delta F_{298}^0 = -92,760$ cal. for propionic acid.

The standard free energy of formation of water has been calculated by Lewis and Randall (10) and found to be $-56,560$ cal. at 298.1°K .

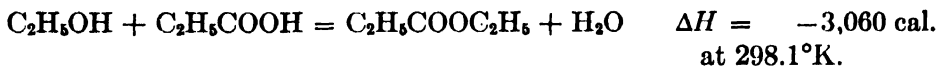
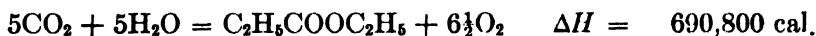
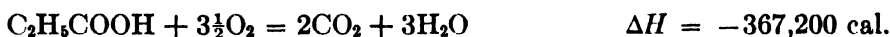
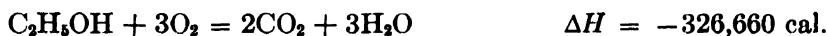
Using these values, the standard free energy of formation of ethyl propionate was calculated to be $-79,634.6$ cal. at 298.1°K .

F. Heat of the liquid reaction

The heat of the reaction in the liquid state was obtained at 298.1°K. from the heats of vaporization of the various constituents as previously calculated, and the ΔH for the reaction taking place in the gaseous state. Combining these algebraically



Kharasch (7) made a general and critical review of the data to be found in the literature for heats of combustion. By using the data of his choice the heat of the esterification reaction in the liquid state was calculated as follows:



Kharasch estimated that the figures to be found in the literature for the heats of combustion may be in error by 1.0 to 1.5 per cent. It is to be noted that the value of the heat of the esterification reaction calculated from the heats of combustion of the several constituents of the reaction agrees with the heat of the reaction calculated from the equilibrium constants determined in this work, within the 1.0 per cent error involved in the heat of combustion data.

G. Entropy of ethyl propionate

Because of the 1 per cent error that may exist in the determined value of the heat of combustion of ethyl propionate, the entropy of ethyl propionate calculated by means of the equation

$$\Delta F^\circ = \Delta H - T\Delta S^\circ$$

can be considered as no more than an approximation. Using $-121,950$ cal. as the heat of formation of ethyl propionate

$$\Delta S_{298.1}^0 = -141.95 \text{ cal.}$$

and

$$S_{298.1} = 70.04$$

DISCUSSION

It is believed that the heat of this reaction calculated from the temperature coefficient of the free energy change is considerably more accurate than that calculated from the data on heats of combustion. It is significant to note that for the esterification of acetic acid and ethyl alcohol studied by Essex and Clark, the more accurate combustion data for alcohol now available (13) give a heat of reaction much closer to the value they determined. Thus, ΔH for the liquid reaction as determined by Essex and Clark is 4795 cal.; from combustion data available at the time of their work it is 1630 cal.; using the more accurate combustion data for alcohol now available it is 3520 cal.

Moreover, the free energy change for this esterification reaction determined by this method should exceed appreciably in accuracy values which may be obtained, when all the data are available, from the entropies or free energies of the reactants and resultants, for the following reasons:

(1) Kürti (9) and Giauque (4), who have attained very low temperatures by means of the demagnetization of paramagnetic substances, have obtained a C_p - T curve at low temperatures for $\text{Gd}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$ which is very different from the curve obtained by extrapolation using the Debye formula. Hence it appears that entropy values calculated by use of the area under such extrapolated curves may be appreciably in error.

(2) In getting the free energy of formation of each compound from the relation

$$\Delta F = \Delta H - T\Delta S$$

ΔF is the difference between two quantities which are often of comparable magnitude, resulting in a large percentage error in ΔF .

(3) In obtaining the free energy change for the reaction from the relation

$$\Delta F = (\Delta F_3 + \Delta F_4) - (\Delta F_1 + \Delta F_2)$$

ΔF is again the difference between two quantities of comparable magnitude for reactions which reach an easily measurable equilibrium, and is therefore subject to a large percentage error. On the other hand, this same situation must make for a small percentage error in the value of the free energy of any one of the reactants or resultants obtained from a determined value of the free energy change of the reaction by use of the above relation.

SUMMARY

1. Equilibrium has been reached in the gaseous phase for the system propionic acid, ethyl alcohol, ethyl propionate, and water, approaching it by a dynamic method from both sides at three temperatures, 428.1°K., 443.1°K., and 473.1°K.

2. The activity ratio K_a has been calculated by means of the gaseous state equilibria to be:

T , °K.....	298.1	298.1	428.1	443.1	473.1
State.....	Liquid	Gas	Gas	Gas	Gas
K_a	8.03	365.3	30.85	26.29	20.00

3. The standard free energy changes for the esterification reaction calculated from the determined activity ratios are:

T , °K.....	298.1	298.1	428.1	443.1	473.1
State.....	Liquid	Gas	Gas	Gas	Gas
ΔF° , cal.....	-1234.6	-3497.8	-2919.2	-2880.5	-2818.3

The standard free energy of formation of ethyl propionate in the liquid state at 298.1°K. is calculated to be -79,634.6 calories.

4. From the curve for the change of K_a with temperature, the heat of the esterification reaction has been calculated for the gaseous state at 431.0°K. and 466.3°K. For 298.1°K. it was calculated from Kirchoff's equation for the gaseous state, and from the vapor pressure and heat of the gaseous reaction for the liquid state.

T , °K.....	298.1	298.1	431.0	466.3
State.....	Liquid	Gas	Gas	Gas
ΔH , cal.....	-5627.4	-5397.8	-4386.7	-4264.8

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THE THERMAL CHEMISTRY OF *d*-GLUCOSE AND OTHER GLUCOSE SUGARS IN SODIUM HYDROXIDE SOLUTIONS

B. CLIFFORD HENDRICKS

Department of Chemistry, University of Nebraska, Lincoln, Nebraska

AND

WARREN H. STEINBACH

Department of Chemistry, University of Arkansas, Fayetteville, Arkansas

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A great many methods of studying the behavior of sugars in solutions have been used by students of sugar chemistry. A very complete catalogue and bibliography of such techniques has but recently been published (13). The authors wish to suggest in this paper still another plan of following the changes of sugars in solution.

Some work on the thermal properties of glucose and its derivatives, reported previously (1), gives values for the heats of solution (9, 14), and some earlier workers (2, 4) attempted to measure the heat of mutarotation of glucose. Evans and students (6) have varied the concentration of alkali used and the temperature of the reaction in an effort to interpret the mechanism of such reactions. In this study the concentration of the alkali in which the sugar was dissolved was varied, and the quantity of heat evolved was measured for each variation.

METHOD, APPARATUS, AND SUGARS USED

The measurements here reported were made in an adiabatic calorimeter in a manner much as previously described (11, 6). However, instead of placing water in the Dewar flask, sodium hydroxide solution of the proper concentration was placed in it. The reciprocating stirrer used did not appreciably agitate the surface of the solution, consequently the air present in the solution was scarcely more than that which entered by diffusion. As the concentration of the alkali solution became greater, a heat of stirring was noted. Proper corrections were applied, in such cases, to the temperature data for this energy. At the higher concentrations some heat was evolved after the principal evolution of heat had stopped. It was not difficult to determine the point of inflection between the temperature-time curve of this second evolution of heat and the temperature-time curve resulting from the first introduction of the sugar. Such point of

inflection was always considered the end of the reaction, thermally speaking. The average times of reaction for the sugars were as follows: *d*-glucose, 38 min.; α -*d*-glucose, 30 min.; β -*d*-glucose, 33 min.; and α -methyl-*d*-glucoside, 29 min., although six of the twelve experiments with this glucoside were of only 10 min. duration.

The *d*-glucose, β -*d*-glucose, and α -methyl-*d*-glucoside were prepared and had the properties previously described (9). The α -*d*-glucose had a rotation of $[\alpha]_D^{20} = +110.1$ and was prepared by the method of Hudson and Dale (12). (Throughout this paper wherever the term "*d*-glucose" is used

TABLE 1

Heat of reaction of crystalline d-glucose with sodium hydroxide at $25.2^\circ \pm 0.3^\circ\text{C}$.

EXPERIMENT NO.	ALKALI NORMALITY	Δt	W ₁ WEIGHT OF SUGAR SAMPLE	W ₂ WEIGHT OF ALKALI SOLUTION	CALCULATED HEAT OF REACTION	AVERAGE HEAT OF REACTION	ALKALI ABSORBED PER MOLE OF SUGAR	HEAT OF NEUTRALIZATION OF ABSORBED ALKALI
	<i>N</i>	$^\circ\text{C}$.	grams	grams	Cal. per mole	Cal. per mole	moles	Cal. per mole
90	0.483	0.0673	3.76	997	6.14	} 6.15	0.055	0.7
91	0.483	0.0629	3.47	986	6.16			
92	0.996	0.0732	3.29	1013	6.65	} 6.61	0.295	4.1
93	0.996	0.0478	2.28	1021	6.57			
94	1.988	0.0746	3.26	1039	7.06	} 7.03	0.558	7.7
95	1.988	0.0801	3.55	1037	6.99			
96	3.054	0.0725	3.14	1094	7.28	} 7.27	1.242	17.0
97	3.054	0.0493	2.12	1089	7.26			
98	4.635	0.0517	2.15	1146	8.07	} 8.06	1.134	15.6
105	4.635	0.0428	1.57	1099	8.03			
137	6.229	0.0330	1.09	1188	8.95	} 8.99	0.990	13.6
128	6.229	0.0322	1.05	1190	9.02			

the equilibrium mixture with $[\alpha]_D^{20} = 52.5$ is meant.) The sodium hydroxide solutions were prepared from Mallinckrodt's c.p. quality stick sodium hydroxide in carbonate-free water.

EXPERIMENTAL

The heat capacity of the calorimeter vessel (10) was 123.3 cal. This value was checked by an alternative method, using the heat of neutralization of sodium hydroxide by hydrochloric acid at 25°C . (16). The heat of reaction is defined in kilogram-calories per mole of sugar. It is calcu-

lated as the total heat of the reaction corrected for heat of solution (9, 10) of the sugar under test.

The heats of reaction of *d*-glucose with sodium hydroxide solutions of varying concentration are given in table 1. After a determination for

TABLE 2

*Heat of reaction of α -*d*-glucose with sodium hydroxide at $25.1^\circ \pm 0.3^\circ\text{C}$.*

EXPERI- MENT NO.	ALKALI NORMAL- ITY	$^\circ\text{C}$.	W ₂ WEIGHT OF SUGAR SAMPLE	W ₂ WEIGHT OF ALKALI SOLUTION	CALCU- LATED HEAT OF REACTION	AVERAGE HEAT OF REACTION	ALKALI ABSORBED PER MOLE OF SUGAR	HEAT OF NEUTRALI- ZATION OF ABSORBED ALKALI
					Cal. per mole	Cal. per mole	moles	Cal. per mole
133	0.247	0.0477	3.21	994	5.47	5.49	0.072	0.99
134	0.247	0.0468	3.11	995	5.51			
26	0.523	0.0488	2.20	1010	6.56	6.48	0.216	2.96
25	0.523	0.0497	2.35	1010	6.48			
24	0.523	0.0444	2.15	1010	6.41			
22	1.039	0.0474	2.50	1032	6.66	6.67	0.378	5.18
21	1.039	0.0407	2.15	1027	6.68			
20	2.124	0.0451	2.34	1067	6.93	6.91	0.648	8.91
19	2.124	0.0500	2.25	1071	6.95			
18	2.124	0.0551	2.52	1069	6.86			
16	3.145	0.0490	2.22	1105	7.01	6.99	1.368	18.77
15	3.145	0.0474	2.17	1111	6.97			
14	4.691	0.0496	2.19	1158	7.22	7.23	1.008	13.82
13	4.691	0.0513	2.22	1137	7.24			
12	4.691	0.0510	2.18	1114	7.22			
11	6.045	0.0471	2.28	1188	7.42	7.44	0.738	10.12
10	6.045	0.0613	2.28	1026	7.47			
9	6.045	0.0597	2.38	1093	7.42			
7	7.550	0.0621	2.07	1147	8.34	8.40	0.738	10.12
6	7.550	0.0600	2.06	1203	8.41			
5	7.550	0.0555	1.95	1231	8.39			

each alkali concentration a measured volume of the alkali-sugar solution was titrated against standard hydrochloric acid for alkali absorption. In the last column of the table the heat of neutralization of the alkali so absorbed per mole of sugar is listed, using 13,721 gram-cal. per mole as the heat of formation of water from its ions (17).

TABLE 3

Heat of reaction of β -d-glucose with sodium hydroxide at $25.1^\circ \pm 0.3^\circ\text{C}$.

EXPERIMENT NO.	ALKALI NORMALITY	Δt	W ₁ WEIGHT OF SUGAR SAMPLE	W ₂ WEIGHT OF ALKALI SOLUTION	CALCULATED HEAT OF REACTION	AVERAGE HEAT OF REACTION	ALKALI ABSORBED PER MOLE OF SUGAR	HEAT OF NEUTRALIZATION OF ABSORBED ALKALI
	<i>N</i>	$^\circ\text{C}$.	grams	grams	Cal. per mole	Cal. per mole	moles	Cal. per mole
135	0.247	0.0584	2.61	996	5.47	5.47	0.072	0.99
136	0.247	0.0692	3.11	997	5.46			
27	0.523	0.0518	2.14	1010	6.52	6.46	0.216	2.96
28	0.523	0.0513	2.04	1005	6.39			
29	0.523	0.0476	2.03	1008	6.48			
30	1.039	0.0547	2.09	1026	6.65	6.65	0.486	6.67
31	1.039	0.0528	2.11	1025	6.65			
33	2.124	0.0649	2.20	1064	6.88	6.87	0.594	8.15
34	2.124	0.0641	2.19	1071	6.86			
35	3.145	0.0591	2.01	1110	7.01	6.99	1.224	16.74
36	3.145	0.0592	2.03	1110	6.97			
37	4.691	0.0658	2.22	1160	7.19	7.19	0.990	13.58
38	4.691	0.0683	2.30	1155	7.19			
39	6.045	0.0630	2.09	1195	7.38	7.39	0.810	11.11
40	6.045	0.0635	2.11	1195	7.40			
131	7.542	0.0693	2.01	1218	8.36	8.32	0.550	7.54
132	7.542	0.0626	1.84	1221	8.28			

TABLE 4

Heat of reaction of α -methyl-d-glucoside with sodium hydroxide at $25.2^\circ \pm 0.3^\circ\text{C}$.

EXPERIMENT NO.	ALKALI NORMALITY	Δt	W ₁ WEIGHT OF SUGAR SAMPLE	W ₂ WEIGHT OF ALKALI SOLUTION	CALCULATED HEAT OF REACTION	AVERAGE HEAT OF REACTION	ALKALI ABSORBED PER MOLE OF SUGAR
	<i>N</i>	$^\circ\text{C}$.	grams	grams	Cal. per mole	Cal. per mole	moles
55	0.525	0.0072	2.64	961	1.17	1.17	None
56	0.525	0.0074	2.76	962	1.16		
53	1.039	0.0126	2.51	1021	1.67	1.68	None
54	1.039	0.0129	2.53	1009	1.68		
57	2.124	0.0201	2.42	1035	2.35	2.35	None
58	2.124	0.0203	2.45	1044	2.35		
59	3.145	0.0219	2.47	1097	2.52	2.53	None
60	3.145	0.0234	2.62	1097	2.54		
61	4.692	0.0245	2.55	1131	2.72	2.72	None
62	4.692	0.0252	2.66	1159	2.72		
63	6.045	0.0294	2.47	1148	3.22	3.22	None
64	6.045	0.0318	2.67	1148	3.22		

Tables 1 to 4 give the following data: the normality of the alkali; Δt , the change in temperature; W_3 , the weight of the sugar sample; W_2 , the weight of alkali solution used; the calculated heat of reaction; the average heat of reaction; the moles of alkali absorbed per mole of sugar; and the heat of neutralization of the absorbed alkali per mole of sugar.

DISCUSSION

The quantity of sodium hydroxide absorbed in each experiment was determined in an effort to account for the heat evolved in the reaction. A study of tables 1, 2, and 3 and figure 1 suggests three energy factors operating in these experiments: one, which is exothermic, in the absorp-

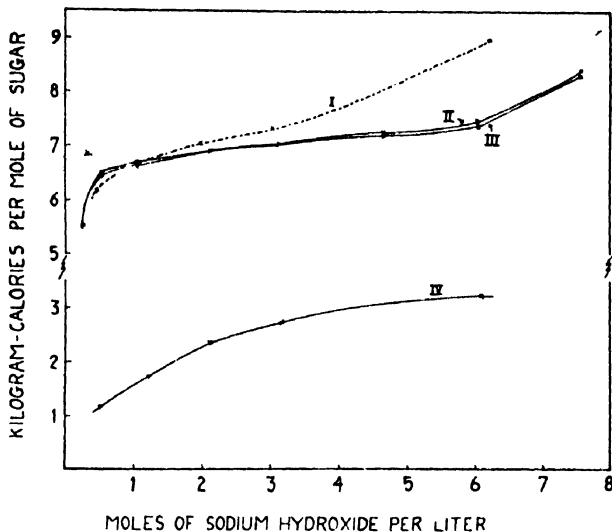


FIG. 1. Summary of the heats of reaction curves. I, crystalline *d*-glucose; II, crystalline α -*d*-glucose; III, crystalline β -*d*-glucose; IV, crystalline α -methyl-*d*-glucoside.

tion or neutralization of the sodium hydroxide; another which, at lower alkali concentrations, is of sufficient exothermic magnitude to add to the heat of neutralization of the alkali; and a third, evident above 2 *N* alkali concentration, which is sufficiently endothermic to render the heat of reaction less than the heat of neutralization. Another indication of the character of the changes in the sugar at higher alkali concentrations is the drop in alkali absorption above 3 *N* concentration. One interpretation of this drop may be that it is due to a decrease in the amount of hydrogen-ion-yielding products formed in the alkali-sugar reactions.

The work of Shaffer, Urban, and Williams (20, 21) quite definitely shows *d*-glucose as a source of hydrogen ions in water solutions. Their work also states that α -methyl-*d*-glucoside exhibits no acidity (21), just as

table 4 indicates no alkali absorption. It is not possible to use their data in checking this work, however, since their lowest concentration of sugar was 0.1 *M*, while the highest concentration used here was 0.017 *M*.

The increased heat of reaction with increased alkalinity for the first three sugars studied may, in part at least, be attributed to the following factors: (1) greater interconversion of the de Bruyn and van Ekenstein type at higher alkalinity (5), and (2) the increased tendency to form products of the saccharinic acid type at the higher alkalinities with the resulting greater heat of neutralization of the hydrogen ion.

In relation to the first of the above suggestions, the heats of reaction of *d*-mannose ($[\alpha]_D^{20} = -14.3$) and *d*-fructose ($[\alpha]_D^{20} = -91.7$) with 3 *N* to 6 *N* sodium hydroxide solutions have been found (18) to be 1.14 ± 0.16 Cal. per mole and 3.19 ± 1.06 Cal. per mole, respectively, greater than that of *d*-glucose ($[\alpha]_D^{20} = 52.5$) under the same conditions. An examination of the papers of de Bruyn and van Ekenstein (5) indicates a larger conversion of *d*-glucose to *d*-mannose and *d*-fructose at higher concentrations of the alkali. The application of this fact to this study would seem justifiable.

The increased heat of reaction of α -methyl-*d*-glucoside with increased alkalinity may not be accounted for as above. The fact that its rather constant heat of reaction is less than that of *d*-glucose, α -*d*-glucose, and β -*d*-glucose may be attributed to its negligible formation of hydrogen ions. It would seem that the acidity found by Shaffer, Urban, and Williams must be due largely to the first carbon atom of the sugar molecule, since the methyl group has so completely depleted such ionization.

The heat of reaction of α -*d*-glucose (in table 2) is an average of 0.03 Cal. per mole more than that of β -*d*-glucose (table 3). While this difference is not significantly greater than the experimental error of these measurements, it is a difference which, if found at all, always shows a greater heat of reaction for α -*d*-glucose.

Recent investigations indicate that there is a measurable heat of mutarotation of β -*d*-glucose to α -*d*-glucose. Isbell and Pigman (13) report the specific rotation for *d*-glucose in water solution to be $[\alpha]_D^{20} = 52.7$ and $[\alpha]_D^{0.2} = 52.1$. This would indicate that there is a heat of mutarotation of 0.06 Cal. per mole absorbed by the β -form in changing to the α -form. Sturtevant (19), by direct calorimetric measurement, gives the heat of mutarotation for α -*d*-glucose, in 5×10^{-5} *N* hydrochloric acid, as 0.16 Cal. per mole. While these values do not agree quantitatively, they do support each other as to the existence and the sign, i.e., direction of absorption, of this energy factor. In an analysis of heats of reaction in this investigation this factor should be considered.

The foregoing interpretation does not account for the difference in the heats of the reaction of *d*-glucose as compared with those of α -*d*-glucose

and β -*d*-glucose. If *d*-glucose, as has been generally considered, is purely an equilibrium mixture of the α - and β -*d*-glucoses, then there is no reason to expect any difference between energies of reactions for any two of these sugars. But the findings of this research do not present such an identity. The authors consider this failure of their data to support such an identity to warrant doubt that *d*-glucose is as simple as a two-component system. In a previous communication (9) they pointed out that the heat of solution for crystalline *d*-glucose ($[\alpha]_D^{20} = 52.5$) does not duplicate the heat of solution of the generally accepted 2:1 mixture of β -*d*-glucose with α -*d*-glucose. They submit these two independent sets of data as warrant for more than a passing interest in the statement (15): "we must suppose that the proportion of furanose sugar is by no means negligible even in solutions from which only alpha and beta pyranose sugars can be separated by crystallization."

Changes due to oxidations, other than autooxidation, are not considered of importance in these experiments for two reasons: first, the duration, 30 min. more or less, of the individual runs at the highest alkalinity, 6 *N*, is known (3) to destroy less than 0.5 per cent of the sugar even if air is bubbled continuously through the solution. This per cent would obviously be much less at lower concentrations and would probably, in no case, be that great, since air by diffusion into the solution would be much less than if it were forced through, as was the case in Boscult's work. Second, the bromine oxidation rate of β -*d*-glucose is about thirty times that of α -*d*-glucose (13). The authors, in this research, found no appreciable difference in the reaction rates for these two sugars. This means that if there is any oxidation in these reactions its effect is entirely masked by other factors. They recognize that oxidations by air (3) or copper acetate (7) are much less rapid than by bromine (13), which would, in turn, minimize the energy contribution of this factor in these experiments.

SUMMARY

1. Heats of reaction with sodium hydroxide, at six or more different alkali concentrations, have been determined for *d*-glucose, α -*d*-glucose, β -*d*-glucose, and α -methyl-*d*-glucoside.

2. Heats of reaction for all four sugars increase with increased alkali concentration.

3. Heats of reaction for α -*d*-glucose are consistently, though only slightly, higher than those for β -*d*-glucose.

4. Heats of reaction for *d*-glucose at alkali concentrations above 2 *N* are increasingly greater with increasing alkali concentration than those of α -*d*-glucose and β -*d*-glucose.

5. The heats of reaction for α -methyl-*d*-glucose for all concentrations of the alkali above 0.5 *N* are 4.52 ± 0.42 Cal. per mole less than the corresponding heats of reaction of the α - and β -*d*-glucoses.

6. Salt formation with the alkali seems to be the major source of the heat measured.

7. Increased heat of reaction with increased alkali concentration is attributed to influence of alkali upon the de Bruyn-van Ekenstein inter-conversion of *d*-glucose, α -*d*-glucose, and β -*d*-glucose.

8. The departure of the heats of reaction for *d*-glucose from those of the α - and β -*d*-glucoses is considered possible evidence for other components than the α - and β -*d*-glucoses in crystalline *d*-glucose.

9. The adiabatic calorimeter is recommended for use along with the polarimeter, the dilatometer, and the refractometer in the study of sugar solutions and their reactions.

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ALKALI ADSORPTION BY SYNTHETIC RESINS

E. I. AKEROYD¹ AND GEOFFREY BROUGHTON

*Department of Chemical Engineering, Massachusetts Institute of Technology,
Cambridge, Massachusetts*

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In spite of the great industrial importance and common use of the phenol-formaldehyde resins, it was not until 1935 that attention was drawn to their adsorptive properties and possible use as water softeners (1). This appears somewhat surprising, since it might be expected that some, at least, of the phenolic hydroxyl groups will remain active after condensation, serving as active centers for adsorption. Thus, although attention had been called to the amphoteric properties of phenol formaldehyde resins (9), and Shono (11) had examined the behavior of metallic salts reacting with phenolic resins to give colored products, the first systematic adsorption experiments were made by Adams and Holmes (1), using a flow method. The solution under examination was allowed to pass down a column packed with the resin, and, although difficulties due to channelling made the results only semiquantitative in nature, strong selective adsorption in acid solution was shown by catechol, resorcinol, quinol, pyrogallol, and catechin resins and general adsorption by phloroglucinol and quebracho tannin resins. In alkaline solution marked adsorption of cations occurred, varying considerably with the nature of the phenol present. Amine-formaldehyde resins showed adsorption in acid solution. Ellis (4) has stated that a wide variety of phenols of high molecular weight and of natural origin may be condensed with formaldehyde to give products which will remove cations from dilute aqueous solution. Complete removal of dissolved salts, therefore, may be accomplished by treatment with a phenolic resin to remove cations followed by an amine-aldehyde resin to remove anions (1). Since many of the resins can be produced at economical prices, their application to water treatment is obvious and appears to have commercial possibilities. The present investigation was an attempt to elucidate the mechanism of the adsorption process and the relation of the molecular structure of the resins to their adsorptive power. For this purpose the adsorption and rates of adsorption of calcium hydroxide and three other bases by simple mono-, di-, and tri-hydroxy phenol resins were measured. The results should be

¹ Fellow of the Salters' Institute of Industrial Chemistry, London, England.

of value in the study of resins made from more complex, naturally occurring phenols, which are of greater utility in commercial water softening.

PROCEDURE

A. Preparation of resins

Two parts² of phenol, 20 parts of water, and 4 parts of formalin (40 per cent) were heated to boiling and 1 part of concentrated hydrochloric acid in 2 parts of water was added. The resin separated almost immediately and was filtered and washed, first with boiling water, then with aqueous calcium hydroxide solution until the filtrate became colorless. The resin was regenerated by washing several times with 5 per cent hydrochloric acid, followed by water, alcohol and ether. After drying at 100°C. it was crushed and graded through 48 mesh on to 200 mesh.

In most preparations the resin was precipitated on 2 parts of kieselguhr, added to the mixture before the catalyst. Subsequent procedure was the same as for the pure resin, but analyses were made for water and organic content. The presence of kieselguhr resulted in a smaller loss in fines on grading the resin.

B. Adsorption measurements

A known quantity of resin was weighed out into a bottle and a known amount of standard calcium hydroxide or other solution added. After agitation for a measured time on a rotary shaker at room temperature ($25^{\circ} \pm 2^{\circ}\text{C}.$), the solution was filtered and analyzed. Blanks were run to determine any adsorption by the kieselguhr. This was small, of the order of 0.012 g. of calcium per gram of kieselguhr. This was allowed for when calculating the amount of adsorption. Results were reproducible, within 3 per cent, on different samples of a resin as well as on the same sample and are expressed as millimoles per gram of resin in all cases.

VARIATION OF ADSORPTION WITH ALKALINITY

Adams and Holmes (1) found that the simple phenolic resins did not appear to adsorb cations from neutral solution. Phenol, quinol, catechol, and resorcinol resins behaved similarly with calcium sulfate solution. Even after agitation for three months the adsorption by catechol resin from 0.01 *M* calcium sulfate was only 0.15 millimole per gram of resin.

RATE OF ADSORPTION

Adsorption is relatively slow, apparently becoming almost complete after about seven days, but probably proceeding very slowly over a period of months. In figure 1 are represented the results obtained for various

² All parts are parts by weight.

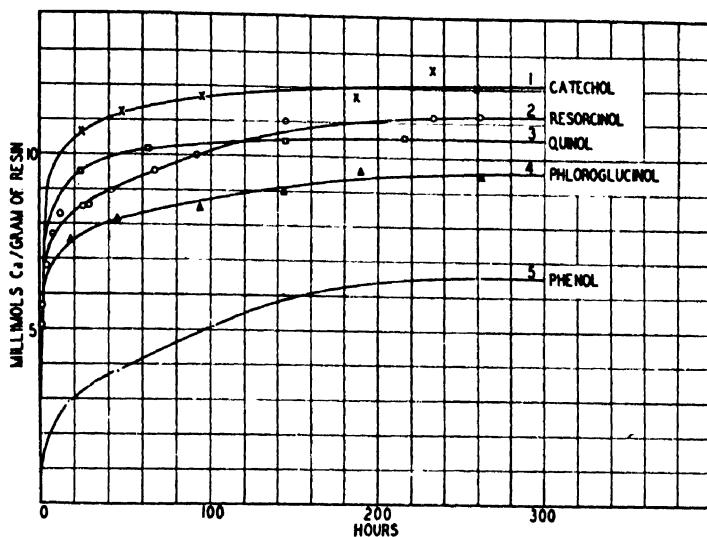


FIG. 1. Rate of adsorption of calcium hydroxide by various resins

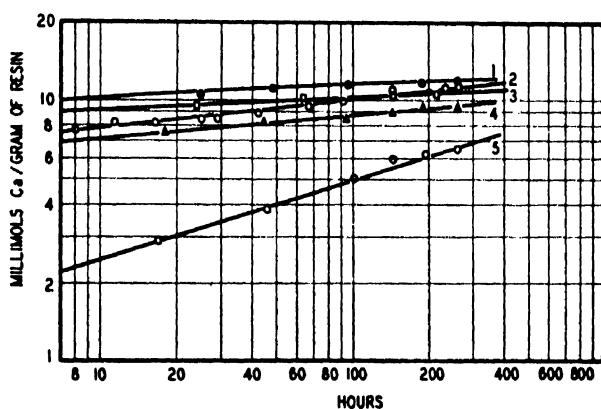


FIG. 2. Adsorption of calcium hydroxide by various resins

TABLE 1

Rates of adsorption by different resins

RESIN	<i>k</i>	<i>n</i>	EQUILIBRIUM ADSORPTION <i>millimoles per gram of resin</i>
Resorcinol.....	11.8	0.12	11.2
Quinol.....	17.0	0.042	10.5
Catechol.....	18.1	0.054	12.1
Phloroglucinol A.....	12.0	0.081	9.6
Phloroglucinol B.....	10.8	0.068	7.9
Phenol.....	2.7	0.29	6.25(approx.)

resins and calcium hydroxide solution. In all these experiments a quantity of sorbent, corresponding to 0.27 g. of resin after correcting for the kieselguhr content, and 500 cc. of 0.0198 *N* calcium hydroxide were taken. The curves, as seen from figure 2, can be represented by an equation of the usual type (6)

$$x/m = kt^n$$

where x/m is the adsorption in millimoles of calcium per gram of resin, t is the time of adsorption, and k and n are constants. The values of the

TABLE 2

Adsorption of calcium hydroxide by a resorcinol resin

0.5175 g. of resin (0.270 g. of organic content) agitated with 500 cc. of calcium hydroxide solution for three months

INITIAL CONCENTRATION OF CALCIUM HYDROXIDE <i>millimoles of Ca per liter</i>	FINAL CONCENTRATION OF CALCIUM HYDROXIDE <i>millimoles of Ca per liter</i>	x/m
99.0	26.2	13.5
148.5	74.5	13.7
198.0	125.0	13.6

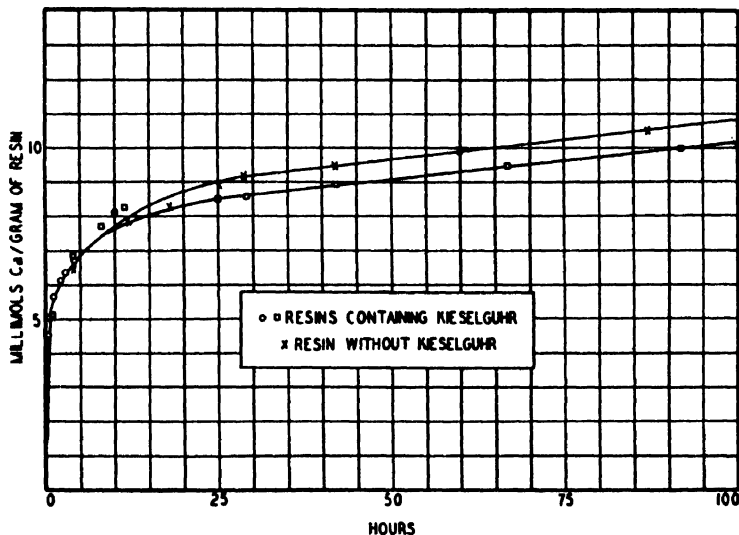


FIG. 3. Adsorption of calcium hydroxide by resins with and without kieselguhr

constants k and n and the equilibrium adsorptions (i.e., the adsorptions at infinite time read from figure 1) for the various resins are tabulated in table 1. Results obtained for a resorcinol resin (table 2) appear to indicate that slow adsorption does occur even after three hundred hours. The equilibrium adsorption value is raised somewhat and is independent of concentration.

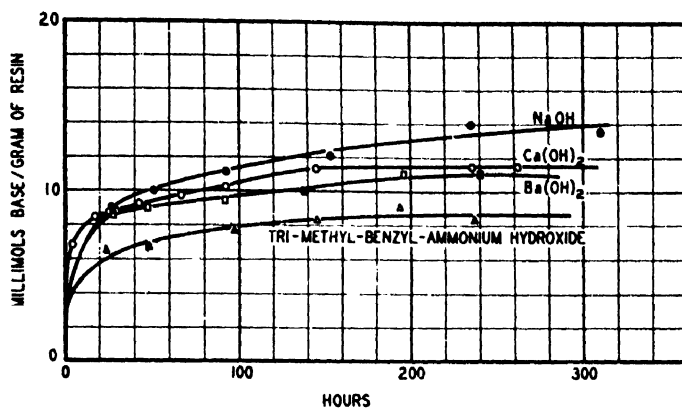


FIG. 4. Adsorption of calcium, barium, sodium, and trimethylbenzylammonium hydroxides on a resorcinol resin containing kieselguhr

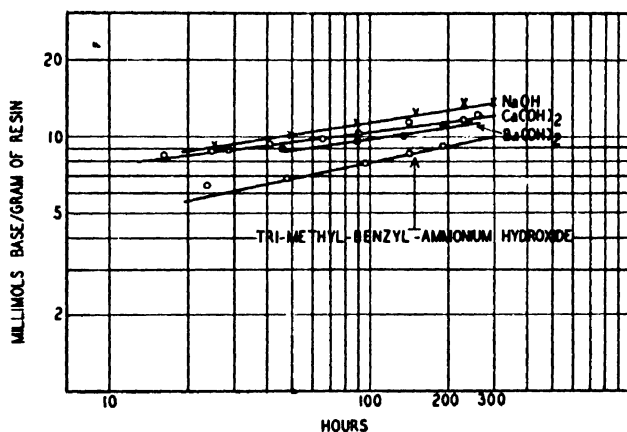


FIG. 5. Adsorption of calcium, barium, sodium, and trimethylbenzylammonium hydroxides on a resorcinol resin containing kieselguhr

TABLE 3

Adsorption of different bases by a resorcinol resin containing kieselguhr

BASE	<i>k</i>	π RATES OF ADSORPTION OF DIFFERENT BASES	π DIAMETER ION IN ANGSTROM UNITS (EQUILIBRIUM ADSORPTION millimoles per gram
Calcium.....	11.9	0.12	1.02	11.5
Barium.....	9.17	0.16	1.37	11.3
Sodium.....	5.09	0.17	0.98	14.0
Trimethylbenzylammonium hy- droxide.....	2.92	0.21	9.0 ¹	8.6

¹ Estimated.

It is surprising to find that incorporation of kieselguhr by direct formation of the resin on it has little effect on the rate of adsorption or the final value attained. Thus, up to about twenty-five hours the curves in figure 3 for resins, with and without kieselguhr, appear to be identical. Above this point they run parallel with a spread of roughly 5 per cent. This may be compared with the finding of Bhatnagar, Hapur, and Puri (2) that different modes of activation had little or no effect on the adsorptive properties of a resorcinol-formaldehyde resin.

A series of experiments were also made with calcium, barium, sodium, and trimethylbenzylammonium hydroxides on a resorcinol resin containing kieselguhr. As before, 500 cc. of 0.0198 *N* base with 0.27 g. of resin (after correcting for kieselguhr content) was used. The results are shown in figures 4 and 5 and are summarized in table 3.

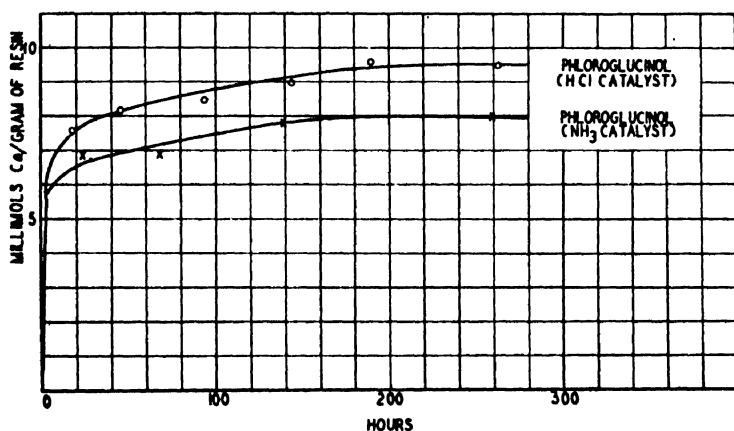


FIG. 6. Adsorption of calcium hydroxide by phloroglucinol resins

EFFECT OF CATALYST ON ADSORPTIVE POWER

The equilibrium adsorption found above for the phloroglucinol resin, in contrast to the results of Adams and Holmes (1), is considerably lower than the equilibrium values for the dihydroxy resins. For this reason samples of the resin were prepared, using different catalysts and conditions. It was found that a phloroglucinol resin prepared using ammonia as catalyst had an even lower adsorptive power than the acid-catalyzed resin (figure 6).

ADSORPTION ISOTHERMS

Bhatnagar, Hapur, and Puri (2) determined the adsorption isotherms of a number of substances on resins of this type. The values they found for a resorcinol resin, apparently prepared by the same method, are, however, very much lower than those found in the present investigation. For

adsorption from 0.1 *N* sodium hydroxide solution their adsorption maximum was approximately 5 millimoles per gram of resin as compared with 14.0 in the present experiments. This may possibly be due to differences in the resins or to insufficient time being allowed by them for their solution to come to equilibrium. Thus they state "the systems were agitated for half an hour and allowed to remain until equilibrium was attained." Their values, in fact, check roughly with those interpolated at two hours from the present rate curves (figure 4). In figure 7 are plotted "adsorption

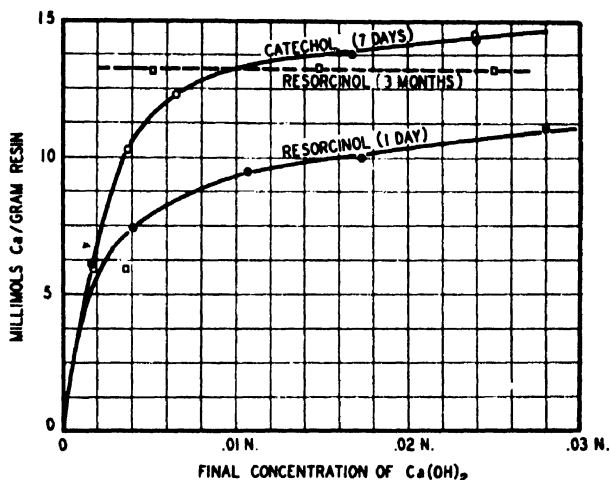


FIG. 7. Adsorption of calcium hydroxide by resorcinol and catechol resins

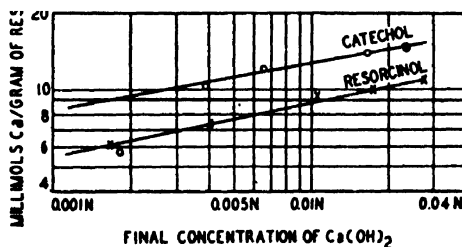


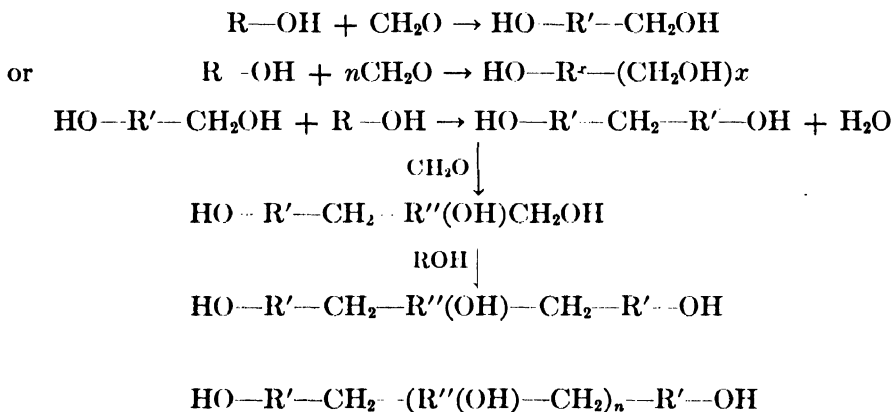
FIG. 8. Adsorption of calcium hydroxide by catechol and resorcinol resins during short times of agitation

isotherms" of resorcinol and catechol resins in calcium hydroxide solution, determined after agitation for one day and seven days, respectively. Points for a resorcinol resin after three months' stirring are also shown. Hence for short times of agitation typical adsorption isotherms are obtained (figure 8), but for long times a curve indicative of chemical combination is observed. The isotherms resemble those for calcium hydroxide and silica gel (7), where there is undoubtedly chemical combination to give calcium silicate.

INTERPRETATION AND DISCUSSION OF RESULTS

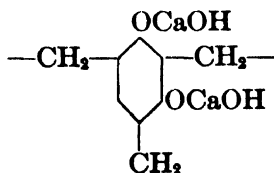
Adsorption of cations in any appreciable quantity is peculiar to the phenol-formaldehyde resins; natural resins and glyptal, vinyl, and ketone-formaldehyde resins show inappreciable adsorption (1). Hence adsorption would seem to be bound up with the phenolic hydroxyl groups and might be expected to be chemical in nature. The present work supports this view.

There is now considerable evidence (7, 10, 8) for the following mode of formation of phenol-formaldehyde resins:



The linear condensation products may further give complex three-dimensional structures by the formation of cross links (4), but in both linear and three-dimensional polymers the phenolic hydroxyl groups are not involved.

Formation of cross links leads to modification of the physical properties of resins, which become harder and more insoluble. Insoluble resins are always formed in the presence of alkaline catalysts although acid catalysts, in the absence of excess formaldehyde, produce soluble Novolak resins, which can only be converted into the insoluble form with excess formaldehyde (6, 1). The resins under investigation are of the insoluble, cross-linked type, excess formaldehyde always being used in their preparation. It is interesting to compare the adsorptions obtained with the values which might be expected on the basis of the above structure, assuming chemical combination to occur between the hydroxide and the base. Taking the basic unit of the dihydroxy phenol resin as $\text{C}_6\text{H(OH)}_2(\text{CH}_2)_{3/2}$, its molecular weight will be 128, there being two hydroxyl groups per unit. Steric considerations indicate that the most probable compound would be



giving a saturation adsorption of 15.5 millimoles of calcium per gram of resin.³ The corresponding figures for mono- and tri-hydroxy phenol resins are 8.9 and 20.8 millimoles per gram, respectively. For a monobasic hydroxide and a dihydroxy phenol resin the saturation adsorption would similarly be 15.5. Tables 1, 2, and 3 show that the resins, with the exception of the phloroglucinol resin, which will be discussed later, approach these maxima. This confirms the predominantly chemical character of the adsorption.

Viewing the adsorption as a chemical reaction, it is necessary to explain the different equilibrium adsorptions obtained for the various resins. Table 3 and figure 4 would also seem to indicate that the size of the adsorbed ion is important, the equilibrium adsorptions being in inverse order to the ionic diameters. This suggests steric hindrance as a factor; different resins may contain hydroxyl groups of varying degrees of accessibility. Again, the calcium ions as they become adsorbed on the resin may affect accessibility of the remaining hydroxyl groups. Models of the resins were constructed; they indicated that the hydroxyl groups in the catechol resin, being in the ortho position, have a tendency to fall into more accessible positions; the links between the benzene rings are on the opposite side to the groups active in adsorption. On the other hand, resorcinol, having a point between the hydroxyl groups at which linkage can occur, forms a structure in which the possibility of shielding the hydroxyl groups is much more likely.

Consideration of figure 7 shows that at seven days the catechol resin possesses higher adsorption values at all concentrations than the resorcinol resin at three months. Furthermore the adsorption measured, 14.5 millimoles per gram, is 94 per cent of the theoretical adsorption maximum.

There remains the anomaly of the phloroglucinol resin, with an adsorption maximum of 19.2 compared to 41.7 theoretically required. This may be attributed, partially at least, to a high degree of polymerization. In phloroglucinol the 2-, 4-, and 6-positions are free, each one allowing substitution in the position ortho to two hydroxyl groups, so that it might be expected that polymerization would occur to a higher degree than in the mono- and di-hydroxy phenols. When the maximum number of cross links are formed the resin offers the maximum steric hindrance to the reaction of the hydroxyl groups; thus a hardened phenol-formaldehyde resin of the Bakelite type does not adsorb cations. Such a pronounced cross-linkage effect would account for the low maximum of the phloroglucinol resin.⁴ A more active catalyst in the resinification might be

³ If there were two $-\text{CH}_2-$ links per benzene ring, the adsorption maximum would be 33. These figures might be lowered somewhat if some calcium atoms were able to satisfy two hydroxyl groups simultaneously.

⁴ The difference might also be accounted for by resinification occurring through the hydroxyl groups, but this appears unlikely (7, 10, 8).

expected to increase the number of cross linkages and hence decrease the adsorptive power of the resin. A resin prepared with ammonia, known to be a very active catalyst (polymerization takes place at room temperature instead of in a boiling solution as with other catalysts), gave a lower adsorption maximum than the acid catalyst resin (figure 6). This observation, that the total possible adsorption is dependent upon the degree of polymerization, is of considerable importance from the commercial standpoint.

The negligible effect of kieselguhr on the rate of adsorption might well be explained by the fact that the amount of kieselguhr employed, 50 per cent by weight, corresponds to only 28 per cent by volume; a larger difference might be detected by the use of a considerably higher volume per cent of kieselguhr. However if, in keeping with the above discussion, it is assumed that the number of available interior hydroxyl groups rather than the number of surface hydroxyl groups govern adsorption, an explanation is at once obvious.

Non-adsorption of calcium sulfate by the resins, the unique behavior of phenolic resins compared with the glyptal, vinylite, and other resins, the results of the adsorption experiments at three months, and the general character of the curves all make it difficult to describe the adsorption as other than chemical. Indeed, the present data can all be explained as a consequence of chemical interaction between the base and the phenolic hydroxyl groups, varying in accessibility in each resin and from resin to resin. Accessibility of these groups, as shown by the amount of base adsorbed, is governed by the structure of the phenol concerned and by the degree of polymerization of the resin.

SUMMARY

The rates of adsorption of calcium hydroxide by some simple mono-, di-, and tri-hydroxy phenol-formaldehyde resins have been determined. The results obtained can be explained on the basis of chemical reaction of the calcium hydroxide with phenolic hydroxyl groups of various degrees of accessibility rather than as a pure adsorption phenomenon.

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STUDIES ON THE LYOTROPIC SERIES. I

THE ADSORPTION OF SALTS ON METHYLCELLULOSE

E. HEYMANN, H. G. BLEAKLEY, AND A. R. DOCKING

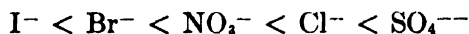
Department of Chemistry, University of Melbourne, Melbourne, Australia

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I. THE LYOTROPIC SERIES

With many phenomena which are influenced by the presence of salts, it is found that if the ions are arranged in the order of their efficiency, they fall into a definite series called the lyotropic series. As examples of such phenomena may be cited the decrease of solubility of gases in liquids on the addition of salts (22), the influence of salts on the solubility, precipitation, or dispersion of hydrophilic colloids (14, 20, 6), the influence of salts on the temperature of the reversible sol-gel transformation and on the swelling pressure of gels (5a). The order of the ions in the lyotropic series is usually CNS^- , I^- , NO_3^- , NO_2^- , Br^- , Cl^- , acetate, tartrate, SO_4^{--} for the more common anions, and Li^+ , Na^+ , K^+ for the univalent cations. Slight variations in this order are often encountered.

It was suggested by Hofmeister that the phenomena are due to the dehydrating action of the ions ("salting out") and their individual affinity for the water molecules, whereby there is a competition between the dissolved molecules or colloidal particles and the ions for the solvent (water). The decrease of the solubility of gases in water caused by the addition of salts may be explained on this assumption. All salts decrease the solubility of inert gases and they act according to the series

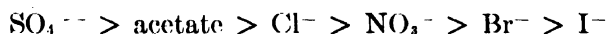


the weakly hydrated I^- causing the smallest, the strongly hydrated SO_4^{--} the largest, depression of the solubility. The explanation would be that the ions with a high energy of hydration, e.g. SO_4^{--} , decrease the hydration of the dissolved molecules more than the ions with a small energy of hydration, e.g., I^- and presumably CNS^- .

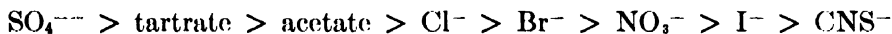
Hofmeister's assumptions contain some features which are characteristic of Debye's theory of the effect of ions on the electric field of the solvent, particularly in the case when the solvent is composed of two kinds of molecules. The bearing of this theory on the problem of the lyotropic action will be discussed in the conclusion.

The action of ions on the solubility and flocculation of hydrophilic colloids cannot be explained on the basis of Hofmeister's simple assumptions. Some salts decrease the solubility of a hydrophilic colloid, whereas others increase it. Generally, it may be assumed that in the case of non-charged or isoelectric hydrophilic colloids flocculation is accompanied by a decrease in the hydration of the particles, and dispersion, or increase of solubility, by an increase. On the basis of Hofmeister's theory only a flocculating and not a dispersing action of ions would be plausible. The dispersing action of weakly hydrated ions such as I^- and CNS^- cannot be explained by this theory.

The same difficulty exists with regard to the reversible sol-gel transformation. In the system gelatin-water, which forms a reversible gel on cooling, SO_4^{--} raises the "melting point" of the gel whereas I^- and CNS^- lower it. In this system the series is (20)



In the system methylcellulose-water, which forms a reversible gel on heating, SO_4^{--} and acetate lower the "melting point," whereas I^- and especially CNS^- raise it, the series being (9, 10)



In both systems the ions at the beginning of the series have solidifying, i.e., presumably dehydrating, action, whereas the ions at the end of the series have liquefying properties and their action is presumably accompanied by an increase of the particle hydration. In this case also, it can be visualized that, according to Hofmeister, ions with a strong energy of hydration, e.g. SO_4^{--} , exert a solidifying influence by their dehydrating action on the particle, but it is not understandable how the weakly hydrated ions CNS^- and I^- can exert liquefying influence. At most it might be expected that they do not influence the solubility or the melting point at all.

I. R. Katz and F. W. Muschter (15) point out that the phenomena in such cases must be the result of more than a salting-out effect. They suggest that an adsorption of ions by the colloidal particles occurs and that the ions at the end of the series, like CNS^- and I^- , are more strongly adsorbed because of their smaller affinity for the solvent than the ions at the beginning of the series, like SO_4^{--} , the latter presumably being either adsorbed very weakly or not at all, because of its strong affinity for water. Thus the weakly hydrated ions CNS^- and I^- increase the hydration of the particles moderately because they carry water molecules with them when adsorbed, whereas SO_4^{--} , although strongly hydrated, does not increase the hydration of the particles because its adsorption is presumably weak. In other words, there is a superposition of the salting-out effect

by an adsorption effect, the former prevailing with the strongly hydrated ions at the beginning of the series, the latter with the weakly hydrated ions at the end. It is significant that in such phenomena where no adsorption or interaction is likely to occur, e.g., the solubility of inert gases, the addition of salts always causes a decrease of solubility, the salting-out effect operating exclusively. On the other hand in such cases where, according to previous experience, adsorption or chemical interaction is possible, e.g., phenomena where interfaces or colloidal molecules with polar groups are involved, the weakly hydrated ions produce an increase of solubility. Here mainly the adsorption effect is operating.

In a recent paper Freundlich and Gordon (5a) suggest that even the lyotropic influence of ions on a complex phenomenon like the swelling pressure of isinglass, CNS^- , I^- , and NO_3^- having an increasing action, SO_4^{--} a decreasing action, may be explained on similar assumptions.

The different magnitudes of adsorption of different ions may be explained on the assumption, that these ions have different affinities for the water dipoles. These affinities may be estimated by the energy of hydration which, for univalent atomic ions, generally increases with decreasing atomic diameter (2, 1, 5). For the halide ions the following values have been obtained: Cl^- , 84; Br^- , 73; I^- , 64 kg-cal., the order agreeing well with the order in the lyotropic series. It can be seen from the measurements of Osaka (18) that the adsorption of potassium chloride, bromide, and iodide on a comparatively inert adsorbent, like charcoal, is determined by the energy of hydration of these ions, the strongest adsorption being exhibited by iodide, which has the smallest energy of hydration, whereas chloride, which has the highest energy of hydration, shows the weakest adsorption.

Unfortunately the energy of hydration is known in a few cases only. In others the magnitude of the hydration itself may be taken as a rough estimate of the affinity between the ions and the water molecules, although it must be remembered that the methods for its determination are still open to controversy.

The magnitude of the adsorption of ions by hydrophilic colloidal particles, however, depends not only on the affinity of the former for water but also on their affinity for the particles, probably owing to the van der Waals attraction between the ions and the polar groups of the particle. The latter may be specific in many cases and depends on the chemical nature of the respective groups. This may cause deviations from the lyotropic series, as usually observed. Such deviations have in fact been frequently found.

In higher concentrations association of ions to molecules occurs, these frequently forming addition compounds with water, e.g., aquo-acids, aquo-bases (16). As a result of this the lyotropic series at higher concentrations may differ from that in dilute solutions. This too has been observed experimentally, e.g., in the system gelatin-water (20).

II. ADSORPTION ON HYDROPHILIC SUBSTANCES

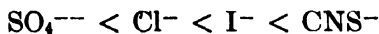
In adsorption processes on hydrophilic colloidal particles, the adsorption of the water molecules, i.e., the hydration, must be taken into account.

It has become customary to determine the adsorption (a) of a solute on an adsorbent from the concentration before (c) and after (c') the process:

$$a = \frac{c - c'}{w} \quad (1)$$

where w is the weight of the adsorbent. In this case it is assumed that no adsorption of the solvent occurs, so that $c - c'$ is positive, if a is greater than zero. If the other extreme is considered, namely that no solute is adsorbed, but that an adsorption of solvent takes place ("solvation"), its molecules in the adsorption layer not being able to act as solvent, c' will be greater than c , and a , which in this case may be called "apparent adsorption," will be negative. In general, both phenomena—adsorption of solute and of solvent—occur with hydrophilic substances. If the former is only slight, the apparent adsorption a , as calculated by equation 1, will be negative. If it increases, a passes from negative values to zero and eventually to positive values, when it outweighs the adsorption of the solvent.

In order to judge the validity of the explanations given for the mechanism of the lyotropic series, it is necessary to obtain more accurate data on the adsorption of salts by lyophilic colloids than have been available up to now. The adsorption of several salts on proteins in solution was measured by Pauli and Matula (21), Northrop and Kunitz (17), and Heymann and Oppenheimer (12), but the investigations were mainly concerned with heavy metal salts. Of the alkali salts only the adsorption of potassium chloride and potassium sulfate on gelatin was determined by conductimetric and potentiometric methods (19, 4), the former showing positive, the latter negative, apparent adsorption. Northrop and Kunitz' measurements of the membrane equilibrium give effects which, in the case of alkali salts, hardly exceed the experimental error. J. A. van der Hoeve (13) measured the adsorption of alkali salts on potato starch and found the series



SO_4^{--} showing negative, CNS^- positive apparent adsorption.

A systematic investigation of the adsorption of various salts on hydrophilic colloidal particles in systems where the lyotropic series is well known with regard to various properties, such as gelatin, agar, methylcellulose, has not yet been carried out.

It is the purpose of this and the following investigations to close this gap.

The system methylcellulose-water is one of the few systems showing reversible gel formation on heating. At low concentrations, where no gel formation occurs, the dissolved substance is precipitated on heating. The methylcellulose gel consists most probably of a fibrous network of particles which are insoluble above 50–55°C. (9). For this reason the adsorption of potassium salts on methylcellulose was investigated at 59°C.

III. THE ADSORPTION OF VARIOUS SALTS ON METHYLCELLULOSE

A. Experimental

In adsorption experiments at an elevated temperature care has to be taken to avoid evaporation losses during filtration of the solution from the methylcellulose with which it has come into equilibrium. To this



FIG. 1. The adsorption vessel

end special adsorption vessels were devised (figure 1). These were made of Pyrex, except for the tap and central tube which were of soda glass. After equilibrium between the solutions and methylcellulose had been attained, the solutions were filtered by connecting the upper end of the tube through a filter medium to a vacuum pipet, the connections being made with rubber pressure tubing. A rapid, and quite efficient, filter was found to be a wad of glass wool packed into a short piece of glass tubing, constricted in the middle.

The adsorption vessels containing the solution and the methylcellulose were placed in an electric thermostat which was maintained at 59.3°C. $\pm 0.1^\circ$ by means of a toluene-mercury electric regulator.

Preliminary experiments showed that the methylcellulose, which was identical with that used by E. Heymann (9), contained a soluble chloride impurity. In order to purify the methylcellulose, it was boiled with successive large quantities (about 3 to 4 liters) of water, being filtered and washed with boiling distilled water between each such treatment.

This was done four to five times and yielded a product which was sufficiently free from soluble impurities. Immediately after the last washing, the methylcellulose was placed in an electric oven at 105–110°C. to dry. The methylcellulose used in the adsorption experiments was recovered, washed well with hot water, and then purified as above.

To facilitate ease of manipulation of the methylcellulose in the actual adsorption experiments, it was in all cases made into small pellets, using a tablet press. These were dried in an electric oven for at least eighteen hours at 105–110°C., after which time they were constant in weight.

The salts used in the adsorption experiments were potassium thiocyanate, potassium bromide, potassium acetate, potassium chloride, potassium sulfate, potassium nitrate, and potassium iodide of "A.R." (B.D.H.) quality.

The adsorption vessel containing 40 ml. of the solution was hung in the thermostat until the solution had reached the thermostat temperature (at least twenty minutes). Then 3 g. of the dry methylcellulose was added. On shaking the pellets broke into a loose mass. The solutions were left in contact with the methylcellulose for at least two days, to attain equilibrium. (In no case was the adsorption found to be appreciably different when solutions of the same concentration were left over longer periods.) Without removing the adsorption vessels from the thermostat, the solutions were then filtered, cooled, and transferred to Jena bottles to await analysis. Usually about 20 ml. of solution was recovered. Adsorption experiments for each concentration were done in duplicate.

Potassium thiocyanate and potassium bromide were analyzed by the Volhard method. Potassium iodide was determined by the same method, with the modifications recommended by Treadwell-Hall (23) to prevent adsorption of potassium iodide by the precipitated silver iodide. Potassium chloride was analyzed by Mohr's method. Copper sulfate was determined by the iodometric method.

Since the convenient methods of estimating sulfate are not very accurate, the potassium sulfate solutions were estimated by evaporating a known weight to dryness in a porcelain crucible, and then heating the potassium sulfate crystals to constant weight in an electric muffle at 610°C.

The potassium nitrate and potassium acetate solutions were converted to potassium sulfate according to the method given by Treadwell-Hall.

These last-mentioned gravimetric methods have the complication that a correction must be made for the weight of the remaining impurities dissolved from the methylcellulose. This was done by evaporating to dryness the filtrates from the experiments with distilled water and methylcellulose, sulfating them, and heating in the muffle to constant weight.

Preliminary experiments showed that the adsorption effects would probably be very small, producing a change in concentration of 1 to 2 per cent

at most. Hence it was decided to supplement the ordinary chemical analysis of the solutions before and after adsorption, by first measuring their conductivities. Since we are dealing with strong electrolytes, we may assume that the equivalent conductivity does not change appreciably in the small concentration range of ± 1 to 2 per cent, and therefore the

TABLE 1

Apparent adsorption of salts by methylcellulose

SALT	(1) APPROXIMATE CONCENTRATION	(2) (3) CONCENTRATION IN MOLES PER LITER		(4) IMPURITY CORRECTION	(5) CORRECTED CONCENTRATION DIFFERENCE	(6) CORRECTED CONCENTRATION DIFFERENCE IN MILLIMOLES PER LITER	(7) PERCENTAGE APPARENT ADSORPTION
		Before adsorption	After adsorption				
KCNS.....	M/10	0.1052	0.1050		+0.0002	-0.2	+0.2
	M/5	0.1925	0.1925		0.0000	0	0
	M/2	0.5130	0.5098		+0.0032	+3.2	+0.6
	M/1	1.035	1.031		+0.0040	+4.0	+0.4
KI.....	M/10	0.0987	0.0989		-0.0002	-0.2	-0.2
	M/5	0.2000	0.2003		-0.0003	-0.3	-0.2
	M/2	0.4991	0.5002		-0.0011	-1.1	-0.2
KBr.....	M/10	0.1001	0.1012		-0.0011	-1.1	-1.1
	M/3	0.3333	0.3368		-0.0035	-3.5	-1.0
	M/1	1.0010	1.0110		-0.0100	-10.0	-1.0
KOOCC ₂ H ₅	M/5	0.2335	0.2365	0.0003	-0.0026	-2.6	-1.1
	M/2	0.5348	0.5411	0.0003	-0.0060	-6.0	-1.1
	M/1	0.9920	1.0038	0.0003	-0.0115	-11.5	-1.2
KNO ₃	M/5	0.1998	0.2030	0.0003	-0.0029	-2.9	-1.4
	M/2	0.5012	0.5072	0.0006	-0.0054	-5.4	-1.1
KCl.....	M/10	0.1006	0.1021		-0.0015	-1.5	-1.5
	M/2	0.5004	0.5076		-0.0072	-7.2	-1.4
	M/1	1.0010	1.0110		-0.0100	-10.0	-1.0
K ₂ SO ₄	M/10	0.1012	0.1033	0.0002	-0.0019	-1.9	-1.9
	M/4	0.2501	0.2549	0.0002	-0.0046	-4.6	-1.9
	M/2	0.5013	0.5089	0.0002	-0.0074	-7.4	-1.5
CuSO ₄	M/10	0.0981	0.0995		-0.0014	-1.4	-1.4

specific conductivities of the solutions are directly proportional to their concentrations.

The conductivity cell used was of the pipet type, made of Jena glass, and of capacity about 16 ml. The cell constant was 0.4063 at 14.20°C. When in use the lower end of the cell was blocked by a piece of rubber tubing sealed with a glass rod.

The interferometer could not be used to measure adsorption, because traces of methylcellulose are soluble in water even at 59°C.

B. Results

In table 1 apparent adsorption is calculated from the results of chemical analysis. Usually, it is expressed as in equation 1

$$a = \frac{c - c'}{w}$$

TABLE 2

Apparent adsorption of salts by methylcellulose, calculated from the conductivity measurements

SALT	CONCENTRATION BEFORE ADSORPTION	SPECIFIC CONDUCTIVITY BEFORE ADSORPTION	SPECIFIC CONDUCTIVITY AFTER ADSORPTION	CORRECTION FOR IMPURITIES	CORRECTED DIFFERENCE OF CONDUCTIVITY	PERCENTAGE CHANGE OF CONDUCTIVITY	TEMPERATURE OF CONDUCTIVITY MEASUREMENT
	<i>equivalents per liter</i>	<i>ohm⁻¹ × 10³</i>	<i>ohm⁻¹ × 10³</i>	<i>ohm⁻¹ × 10³</i>	<i>ohm⁻¹ × 10³</i>		<i>°C.</i>
KCNS.....	0.1049	1.002	1.005	0.003	0.000	0	14.20
	0.1925	1.776	1.783	0.003	-0.004	-0.2	
KI.....	0.0987	1.293	1.297	0.003	-0.001	0	24.25
	0.1998	2.507	2.509	0.003	-0.001	0	
KNO ₃	0.1000	1.184	1.198	0.005	-0.010	-0.8	24.25
	0.2000	2.222	2.248	0.005	-0.021	-1.0	
KCl.....	0.1000	1.029	1.047	0.003	-0.015	-1.5	14.20
	0.2000	1.977	2.007	0.003	-0.027	-1.3	
K ₂ SO ₄	0.1000	1.034	1.055	0.005	-0.016	-1.6	22.30
	0.2000	1.906	1.941	0.005	-0.030	-1.6	

In this case, however, since the same weight of methylcellulose (3 g.) was in each case added to the same volume (40 ml.) of solution, apparent adsorption was simply expressed as

$$a = c - c' \quad (2)$$

where c is the concentration before and c' the concentration after adsorption ("equilibrium concentration"). Column 6 contains this difference in concentration in millimoles per liter. Column 7 is the percentage change of concentration during adsorption per initial concentration, i.e., $\frac{c - c'}{c} \cdot 100$ ("percentage apparent adsorption"). The second and third

columns give c and c' . All concentrations are expressed as moles per liter. The fourth column gives the correction for impurity (i) for those ions which have been determined gravimetrically. This correction must be subtracted from the figures in column 3 to give the true concentrations of those salts concerned. In column 5 ($c - c' - i$) is tabulated as "corrected concentration difference". It has to be remembered, however, that the percentage apparent adsorption is a difference of two concentrations which are not very different. Hence the average error may amount to ± 0.1 to 0.2 unit on the figure obtained.

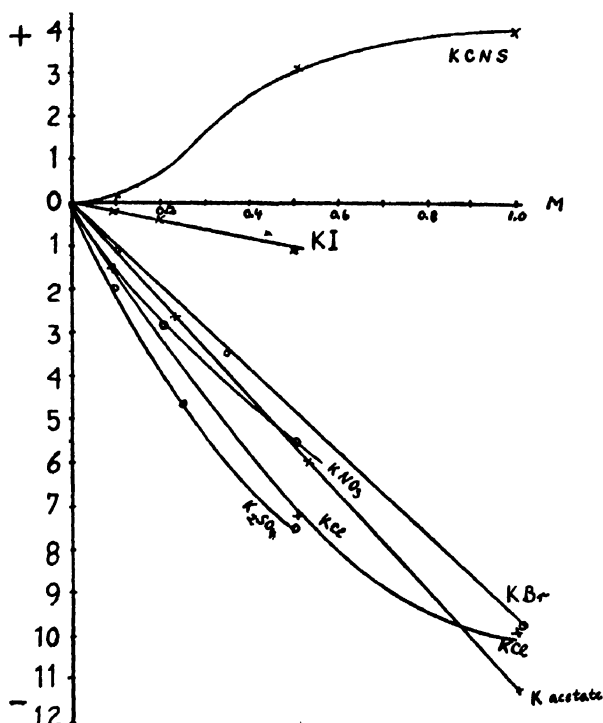


FIG. 2

FIG. 2. Plot of apparent adsorption ($a = c - c'$) against the equilibrium concentration c'

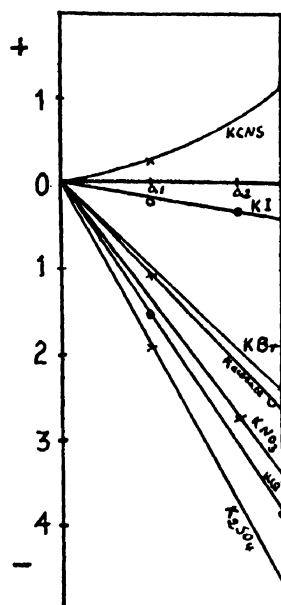


FIG. 3

FIG. 3. Plot of apparent adsorption ($a = c - c'$) against the equilibrium concentration c' at lower concentrations

In table 2 apparent adsorption is calculated from the conductivity measurements as percentage change in specific conductivity (κ). Since for strong electrolytes and small changes of concentration (c)

$$\kappa \sim \text{prop. } c$$

the percentage change in specific conductivity should be approximately equal to the percentage apparent adsorption in table 1.

However, the correction due to the small conductivity of traces of dissolved methylcellulose and impurities is about six to ten times as large as the correction for the gravimetric analysis, whereas in the titrimetric analysis there is no such correction. Consequently accuracy of the value of the percentage apparent adsorption as calculated from the conductivity measurements is much less than that calculated from chemical analysis. For this reason the conductivity results will be merely regarded as confirmatory. A comparison between table 1 and table 2 shows that the values from the conductivity method are slightly less numerically than those obtained by chemical analysis.

In figures 2 and 3 the apparent adsorption $a = c - c'$ is plotted against the equilibrium concentration c' . Only potassium thiocyanate shows positive apparent adsorption, and for potassium iodide apparent adsorption is approximately zero, whereas all the other salts are strongly negatively adsorbed. The difference between the values for apparent adsorption for these other salts is not very marked in concentrated solutions, some of the curves overlapping at higher concentrations (cf. section I). The individual character of the ions is more clearly shown at lower concentrations (figure 3). Potassium sulfate shows the strongest negative apparent adsorption. Then follow potassium chloride and potassium nitrate, which are about equal, and then potassium acetate and potassium bromide. The values for this group of ions from Br^- to SO_4^{--} are, however, not very much different, whereas the values for I^- and CNS^- (zero or positive apparent adsorption) stand far apart from all other ions.

Measurements of the pH of the solutions were made in some cases before and after adsorption. No evidence of an appreciable hydrolytic adsorption was obtained.

IV. THE INFLUENCE OF SALTS ON THE SOLUBILITY OF METHYLCELLULOSE IN WATER

It was decided that an investigation of the influence of salts on the solubility of methylcellulose would prove a useful addition to the results obtained by E. Heymann (9) on the coagulating action of various salts and on their influence on the temperature of the sol-gel transformation.

A few preliminary data were derived from the adsorption experiments where it was shown that the solubility of methylcellulose in water at 59.3°C. is so slight that the accuracy of the determination of adsorption was not affected.

Although the absolute values given in table 3 are small, it can be seen that sulfate has a decreasing, iodide an increasing, effect on the solubility.

It is known that there is an immense increase in the solubility of methylcellulose with decreasing temperature, probably owing to the formation of an oxonium hydroxide. Solubility measurements in water and in salt solutions were therefore carried out at room temperature.

The methylcellulose used in these experiments was not the same as that used for the adsorption experiments, but was material not quite as soluble in water, obtained from the I. G. Farbenindustrie. It was purified by boiling and washing with distilled water. The solubility of this methylcellulose in solutions of the same concentration of various potassium salts was investigated. The concentrations were 1 *M* potassium thiocyanate, 1 *M* potassium iodide, 1 *M* potassium nitrate, 1 *M* and 0.5 *M* potassium chloride, and 0.5 *M* potassium sulfate (1 *M* solution not being obtainable at ordinary temperatures).

TABLE 3

Solubility of methylcellulose at 59.3°C.

	METHYLCELLULOSE grams per 100 ml.	PER CENT OF THE SOLID PHASE DISSOLVED
		per cent
Potassium sulfate (<i>M</i> /5).	0.015	0.20
Water.....	0.028	0.37
Potassium iodide (<i>M</i> /5)..	0.032	0.43

TABLE 4

Solubility of methylcellulose in salt solutions at room temperature

	CONCENTRATION OF SALT	CONCENTRATION OF METHYLCELLULOSE
Potassium thiocyanate.	1 <i>M</i>	2.9
Potassium iodide.....	1 <i>M</i>	2.8
Distilled water.....		1.85
Potassium nitrate.....	1 <i>M</i>	0.70
Potassium chloride....	1 <i>M</i>	0.24
Potassium chloride....	0.5 <i>M</i>	0.60
Potassium sulfate.....	0.5 <i>M</i>	0.23

Ten grams of methylcellulose was packed into each of seven 250-ml. bottles, and 100.0 ml. of the various solutions added, the bottles then being agitated on a mechanical shaker for three days. It was observed that the potassium thiocyanate and potassium iodide solutions were characterized by producing a marked dispersive effect. The supernatant liquid was then filtered through glass wool filters into pipets. Duplicate samples of each filtrate were evaporated to dryness and heated to constant weight in an air oven at 110°C.

In table 4 the concentration of the methylcellulose is expressed as grams of methylcellulose per 100 grams of solution.¹

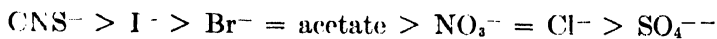
¹ It might have been more reasonable to express the concentration not as grams per 100 grams of solution but as the molar fraction. In this case it would have been necessary to introduce an arbitrary molecular weight for the methylcellulose. The

It can be seen from this table that potassium and potassium sulfate depress the solubility of methylcellulose in water, the order being $\text{SO}_4^{--} > \text{Cl}^- > \text{NO}_3^-$, whereas potassium iodide and potassium thiocyanate increase it. In addition these two last-mentioned ions have a dispersing effect on that part of the methylcellulose which is not being dissolved.

V. DISCUSSION AND CONCLUSIONS

A. *The presumable true adsorption*

We have seen in section III that the apparent adsorption of potassium thiocyanate is slightly positive and that of potassium iodide about zero, whereas all the other ions show negative apparent adsorption. The order is:



with a distinct separation between the CNS^- - I^- group and the other ions. The differences between the ions from Br^- to SO_4^{--} are noticeable, but comparatively small, and they become less significant at higher concentrations.

The fact that the apparent adsorption of potassium iodide is zero cannot be explained on the assumption that no adsorption of iodide occurs, because negative apparent adsorption is found with the ions from Br^- to SO_4^{--} , i.e., water molecules are adsorbed by the methylcellulose particles from a solution containing salt. Consequently the zero apparent adsorption of iodide has to be interpreted on the assumption that iodide is adsorbed as well as water, i.e., that the true adsorption of iodide is positive. Thus thiocyanate shows a still stronger positive true adsorption, since even the apparent adsorption of this salt is positive.

It should be remembered that zero apparent adsorption means that the solute as well as the water is adsorbed in such an amount that the initial concentration remains unchanged. This does not mean, however, that solute molecules and water molecules are adsorbed in equal numbers. Suppose that the apparent adsorption of a 1 per cent molar solution (molar fraction 0.01) is zero. In this case, assuming that both solute molecules and water molecules are being removed from the solution, the ratio of each kind of molecule removed must be one of solute to one hundred of water. In the case of negative apparent adsorption this ratio is still greater. Only in the case of a molar fraction 0.5 are equal numbers of solution molecules and solvent molecules removed, when the apparent adsorption is zero; in all other cases the ratio may be calculated from the

solubility of methylcellulose in the various salt solutions shows such large differences, however, that the order of salts would not be changed if the concentrations were expressed as molar fractions.

molar fraction (cf. Heymann and Boye (11)). There is no difficulty in extending these considerations to ionized solutes.

The negative apparent adsorption of sulfate, which shows the highest value of negative adsorption, can mean that either water is being adsorbed and no solute, or both are adsorbed but the adsorption of the water is so much larger than that of the sulfate that the total concentration is increased. Since the negative apparent adsorption of the ions from Cl^- to Br^- is slightly smaller than that of sulfate, their true adsorption must be slightly higher. However, the fact that the negative adsorptions of all ions from Br^- to SO_4^{--} differ but little suggests that in all these cases the true adsorption is either zero or very small, and that only iodide and thiocyanate show an appreciable positive true adsorption.

B. The hydration of methylcellulose

Assuming that the true adsorption of sulfate is zero, the hydration of the methylcellulose can be calculated from the negative adsorption, since the increase in concentration of the solute during this process will be due to the fact that the adsorbed water molecules responsible for the hydration of the methylcellulose can no longer act as a solvent for the electrolyte. From the values for $M/10$ and $M/4$ solutions (1.9 per cent adsorption for 3 g. of methylcellulose in 40 ml. of solution), the hydration of methylcellulose in the presence of $M/10$ potassium sulfate at 59°C . is 0.25 g. of water per gram of methylcellulose; in salt-free water it may be higher. The corresponding value for gelatin is about 0.30 to 0.50 g. per gram of gelatin, according to the method employed. This hydration value for methylcellulose constitutes a minimum value for the hydration. If a slightly positive true adsorption of sulfate be assumed, the hydration value would be higher. It should be remembered that the experiments have been carried out at 59°C ., hence the hydration of the methylcellulose in the water-insoluble (gel) state is obtained. It may be assumed from measurements of the volume expansion during the sol-gel transformation (Heymann (9)), that the hydration of the methylcellulose in the water-soluble (sol) state at ordinary temperature is several per cent higher.

C. The interpretation of the lyotropic action and the theories of Hofmeister, Debye, and Katz

The ions at the end of the lyotropic series, CNS^- and I^- , which raise the temperature of the sol-gel transformation and increase the solubility of methylcellulose, i.e., which have liquefying properties, show a true adsorption which is much stronger than that of all the other ions. This fact constitutes a strong support for Katz' (15) theory of lyotropic action. Most probably the liquefying properties of CNS^- and I^- are due to adsorption, whereby these ions, although weakly hydrated, increase the

hydration of the colloid, because they carry water molecules with them when adsorbed. On the other hand the experiments show that the true adsorption of all other ions from Br^- to SO_4^{--} is either zero or very small. Consequently no such increase of hydration of the methylcellulose particles can be caused by them. On the contrary they will probably decrease the hydration as a consequence of their affinity for the water molecules, in accordance with Hofmeister's original assumption. The result must be a salting-out effect. In fact, the temperature of the sol-gel transformation of the methylcellulose is lowered (solidifying action) and the solubility in water is strongly depressed in the presence of these ions, the strongly hydrated sulfate having the strongest depressing action. Then follow the more weakly hydrated chloride and then bromide, the energy of hydration of which is still smaller.

Thus the assumption that the lyotropic action is due to (1) a salting-out effect which causes solidification and (2) an adsorption effect which causes liquefaction seems to be in accordance with the experimental results, the first effect operating mainly in the case of the ions at the beginning and the second mainly with those at the end of the lyotropic series.

If the order of the members of the series for the adsorption is compared with that for other phenomena, e.g., precipitation and sol-gel transformation, an irregularity in the position of the acetate is noticed. This ion would be expected to be between chloride and sulfate, whereas it shows about the same apparent adsorption as bromide. This may be due to the

fact that the $\begin{array}{c} \text{O} \\ \parallel \\ \text{—C—} \\ \diagdown \\ \text{O—} \end{array}$ dipole of this organic ion has a special affinity for polar groups of the methylcellulose, causing a stronger positive true adsorption than that expected from analogy to other phenomena (cf. section I).

Since the adsorption effect (and its mechanism) has been fully discussed in section I, it needs no further explanation. A few more words, however, seem to be necessary about the salting-out effect. The competition between ions and colloidal molecules for the water molecules is difficult to visualize, since the water molecules are present in very great excess. A theory of the salting out and the salting in of ordinary molecules in binary liquid mixtures has been proposed by Debye (3), who considered the effect of ions on a solvent which is composed of two kinds of molecules. If the solute decreases the dielectric constant of the solvent, the former will be salted out; if it increases the dielectric constant, it will be salted in. This prediction from Debye's theory has been established experimentally for aqueous solutions of acetone and hydrogen cyanide by P. Gross and his coworkers (7). The effect is due to a separation, the concentration of the

stronger polar molecules being higher in the immediate neighborhood of the ions, whereas that of the less polar molecules is higher at a distance from the ions. This assumption is clearly related to the conception of solvated ions. It is, however, doubtful whether Debye's theory in its original form can explain the lyotropic action even in ordinary solutions. It is true that effects of different magnitude have to be expected for different ions according to their diameter, but it is doubtful, as P. M. Gross (8) has pointed out, whether the theory can explain that the same solute is salted in by some electrolytes, whereas it is salted out by others. Moreover, Debye himself remarks that the electric effect may be only part of the whole and that interaction between the solute and the ion may be important. Besides the latter, the attraction between the molecules of the solute and those of the solvent is not accounted for in Debye's theory.

In the case of solute molecules of colloidal size the departure of the experimental conditions from the idealized assumptions is still greater. It is doubtful, for instance, whether it depends on the dipolar moment of the whole solute molecule or on that of individual groups, whether the solute or the water is more strongly attracted by the ions. Neither the dielectric constant of methylcellulose solutions nor the dipolar moment of this solute has yet been measured. We are at present engaged in measurements of the adsorption of electrolytes on gelatin, in which case the dielectric properties are better known. If the water is the component of higher polarity, an increase of concentration of water dipoles round the ions may be visualized. In the opposite case, however, the assumption of an ion surrounded by colloidal molecules much larger than the ion itself presents considerable difficulties. One would, in this case, rather assume ions surrounding the colloidal molecule. However, even if Debye's theory can be adapted to colloidal systems, it seems highly improbable that the very marked liquefying effects of ions like iodide and thiocyanate can be explained without assuming an interaction between the colloidal molecules and these ions. This assumption seems to be well supported by the adsorption effects found in this investigation.

SUMMARY

1. The adsorption of various salts in aqueous solution on methylcellulose at 60°C. has been investigated. The apparent adsorption is positive for potassium thiocyanate, almost zero for potassium iodide, and negative for all the other salts investigated, the order being potassium bromide, potassium acetate, potassium nitrate, potassium chloride and potassium sulfate, the last showing the strongest negative adsorption. The true adsorption of CNS^- and I^- is considerable, while that of the other ions, in particular of SO_4^{--} , is either zero or very small.

2. From the negative adsorption of potassium sulfate the minimum

hydration of methylcellulose in the insoluble (gel) state has been calculated as 0.25 g. per gram of methylcellulose.

3. The solubility of methylcellulose in water is increased by potassium thiocyanate and potassium iodide and decreased by the other salts, the order being $K_2SO_4 > KCl > KNO_3$. The behavior is analogous to the action of salts on the sol-gel transformation.

4. The results mentioned in paragraphs 1 to 3 show that Katz' theory, assuming a salting-out effect for the strongly hydrated ions and an adsorption effect for the weakly hydrated ones, is a satisfactory basis for the explanation of the lyotropic action. Debye's theory on similar effects for solutes of low molecular weight has also been discussed.

It gives us much pleasure to thank Professor E. J. Hartung for his interest and for providing us with excellent facilities for work in the laboratory.

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MELTING TEMPERATURES OF COMPOUNDS ADSORBED ON SILICA GEL¹

W. A. PATRICK AND W. A. KEMPER

Department of Chemistry, The Johns Hopkins University, Baltimore, Maryland

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INTRODUCTION

One would expect that the capillary forces believed to be responsible for the adsorption of vapors by silica gel would cause a change in the melting temperature of the adsorbed substance. There is already some evidence for this phenomenon in the behavior of the vapor pressure of adsorbed substances at temperatures below their normal melting points. Coolidge (1) found that the vapor pressure isotherms of benzene on charcoal at temperatures below its normal melting point are curves similar to those at higher temperatures. Furthermore, while the latter curves ran asymptotic to the vapor pressure of normal liquid benzene, the former met at a definite angle with the vapor pressure of solid benzene at the same temperature. This lack of phase continuity between adsorbed and solid benzene was still in evidence at a temperature as low as 40°C. below the normal melting point. Patrick and Land (3) measured the adsorption of iodine on silica gel above and below its normal melting point and interpreted their results as indicating a lowering of the melting point of the adsorbed iodine.

Jones and Gortner (2) have measured the freezing temperatures of water on silica gel with a dilatometer. In these experiments the gel and water were covered with toluene and the volume changes on cooling were noted. The thermal contraction of ice, water, and gel were negligible and that of the toluene present was known. The remaining change was attributed to the expansion of water on freezing. Hence the amount of water frozen at each temperature was calculated. They found that as the temperature was lowered more water continued to freeze, and that even at -48°C. there was still 33 g. of unfrozen water per 100 g. of activated gel. They also found a hysteresis effect in that at a given temperature during cooling there was more unfrozen water than at the same temperature during heating. In repeated experiments the same results were

¹ This paper is based on a dissertation submitted by W. A. Kemper to the Board of University Studies of the Johns Hopkins University in partial fulfillment of the requirements for the degree of Doctor of Philosophy, June, 1934.

obtained on heating, only if the cooling had terminated at the same temperature.

Experiments were run with three different concentrations of *gel in water*, but in each case the quantity of water was in excess of that required to saturate the gel. Since this excess froze near 0°C., at lower temperatures there remained saturated gels, all containing the same amount of unfrozen water. Moreover, the results for the amount of unfrozen water at the various temperatures were calculated *per gram of total water present*. However, if the amount of unfrozen water *per gram of dry gel* had been tabulated instead, the results of all three experiments would have been seen to be nearly identical.

The dilatometric method raises two questions. First, what is the effect of immersing the system in toluene? Since the water-toluene interfacial tension is only half that of water-air, larger effects would be expected from capillary forces in the absence of toluene. Secondly, can density changes caused by the negative pressures from these capillary forces be neglected? These negative pressures are greatest on the last-remaining unfrozen water.

Swain and Porter (8) measured the specific heats of argon and hydrogen absorbed on charcoal from 6–50°K. without finding any breaks indicating a sudden change of phase. The specific heats were observed to be less than that of either the solid or the liquid form of these respective elements.

In the present paper a calorimetric method was used to detect any heats of transition attending melting. Specific heats were measured by the Andrews calibrated heat conduction method (5), which is both rapid and continuous. Since it is continuous no intervals are omitted in which a change of phase could escape detection.

APPARATUS AND PROCEDURES

The apparatus is shown in figure 1. The heat is supplied to the calorimeter across an oxygen-filled space separating the calorimeter from an electrically heated, concentric, heavy copper cylinder. The same temperature head is always maintained from the cylinder to the calorimeter, hence the rate of heat transfer to the calorimeter at a given temperature is always the same. Measurements are made of the time required for the temperature of the calorimeter to be raised through successive increments. Two runs with different amounts of a substance of known specific heat give the rate of heat input and the specific heat of the empty calorimeter as functions of the temperature. These functions are used to translate heating times into specific heats of the contents of the calorimeter.

The temperature head and temperature of the calorimeter can be measured by calibrated copper-constantan thermocouples (6) in conjunction with either a White double potentiometer or two type K potentiometers. D'Arsonval galvanometers were used, giving a scale sensitivity of 1.3 to 2.0 mm. per microvolt.

The heat was distributed in the calorimeter can by thirty-four radial fins of 2-mm. brush copper. During a run the temperature at the center of the calorimeter was only 1.5°C . less than at the wall.

An improvement in the apparatus was made by grounding the outer cylinder. This led stray voltages off the thermocouples and the anomalous results previously found (5) at 0°C ., where the thermocouple voltage changes sign, were not experienced. Another modification was the chromium plating of the outside of the calorimeter and of the inside of its containing cylinder.

Identical preparations were made for each run. The calorimeter can and the space between the can and the outer cylinder were rinsed three times with boiling acetone, then dried by heating in a current of dry oxy-

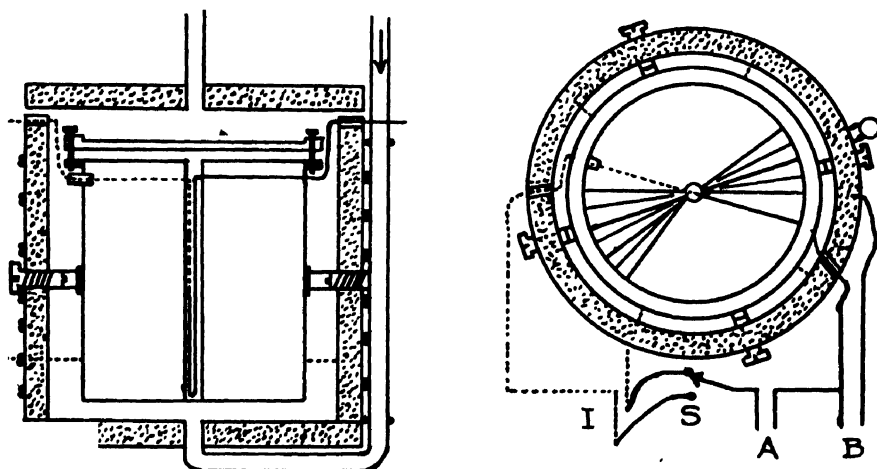


FIG. 1. Vertical cross section of the calorimeter and view from above. I, ice junctions; A, leads to potentiometer indicating temperature at center with knife switch S in upper position and of the wall when in lower position; B, leads to potentiometer for average temperature head. ($\frac{1}{4}$ actual size.)

gen. The calorimeter was then filled and sealed, and the space between the cylinders was swept with oxygen for another half-hour before cooling to the starting temperature. It is essential that the rubber tubing on the inlet oxygen line does not give off condensable vapors. It was found economical to cool first with half a pound of solid carbon dioxide before adding liquid oxygen. When cooling was completed, the inlet oxygen valve was closed and a large heating current was applied until the 1000 microvolt head was obtained. Then, while this temperature head was carefully maintained by manipulation of the vernier adjustment of a series resistance, the times required for each increase of 100 microvolts in the temperature of the calorimeter can were measured with stop watches.

Naphthalene was used as the empirical standard for the calibration.

Wherever available Southard's values (7) for its specific heat were used. Two sets of runs with 22.4 and 71.62 g. of naphthalene gave the rate of heat transfer to the calorimeter and the heat capacity of the empty calorimeter as functions of the temperature.

Silica gel from the Silica Gel Corporation of America was purified by digestion in nitric acid on a steam bath for several days. It was then thoroughly rinsed many times with distilled water during several weeks and finally dried in an oven at 110°C.

The gel was activated by heating for about eight hours at 360°C. in a stream of dried air. The weight of water per unit weight of anhydrous gel was then 3.25 per cent. In this paper the term "activated gel" will represent gel of this water content.

TABLE 1
Amounts of gel and sorbate in experiments

EXPERIMENTS	FIGURES	SILICA GEL	SORBATE	WEIGHT OF SORBATE
		<i>grams</i>		<i>grams</i>
52	2	73.63	Naphthalene	35.96
37, 38, 39, 40, 42, 43	8	48.75	Naphthalene	22.9
57	4	69.22	<i>p</i> -Nitrotoluene	39.26
35	3	52.1	Water	30.1
44 to 48	7	53.3	Water	26.9
19	5, 10	86.6	Benzene	41.8
21 to 24	6	81.3	Benzene	33.2
16	10	82.7	Benzene	25.7
14	10	83.2		0

The sorption was carried out by mixing gel and sorbate in a heated glass-stoppered bottle on a shaking machine for about twelve hours. The shaking was continued until the gel cooled to room temperature. With naphthalene 70°C. was sufficient for rapid adsorption. A higher temperature resulted in a grey discoloration.

OBSERVATIONS

In figures 2, 3, 4, and 5 (see table 1), the observed times of heating are plotted for typical experiments with silica gel and naphthalene, water, *p*-nitrotoluene, and benzene, respectively. In these experiments a little more of the sorbate was present than was necessary to saturate the gel. The melting of this excess can be seen at the indicated normal melting points. There was also a large heat capacity for the system over a wide temperature interval at a lower temperature. This is taken as evidence of the melting of the adsorbed phase. The actual values for the heat

capacity of the adsorbed substance, which are calculated later in this paper, are consistent with this interpretation.

The curves in figures 6, 7, and 8 (see table 1) demonstrate a hysteresis phenomenon. The results were dependent, in the manner shown, upon the lowest temperature to which the system had been cooled previously.

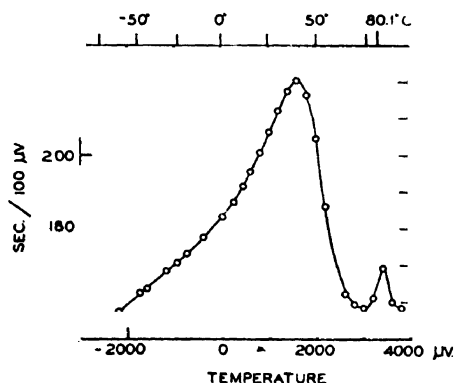


FIG. 2

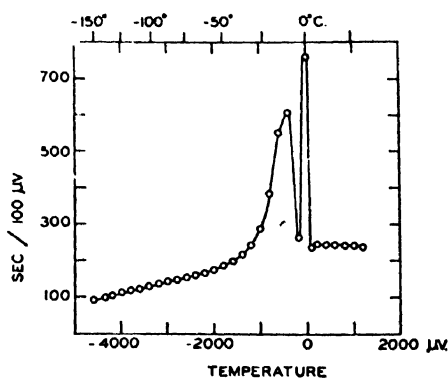


FIG. 3

FIG. 2. Observed heating times for gel saturated with naphthalene and a little excess naphthalene, experiment 52

FIG. 3. Observed heating times for gel saturated with water and a little excess water, experiment 35

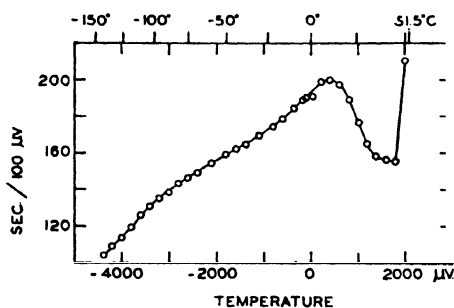


FIG. 4

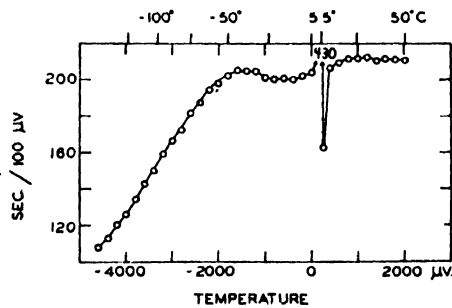


FIG. 5

FIG. 4. Observed heating times for gel saturated with *p*-nitrotoluene and a little excess *p*-nitrotoluene, experiment 57

FIG. 5. Observed heating times for gel saturated with benzene and a little excess benzene, experiment 19

However they were quite reproducible when starting from the same low temperature, and, as far as could be determined, were independent of the rate of cooling or heating.

Figure 9 illustrates how hysteresis in the melting of the adsorbed material could bring about these effects. The slopes of the curves of figure 9,

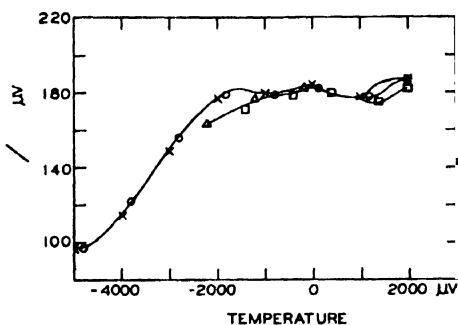


FIG. 6

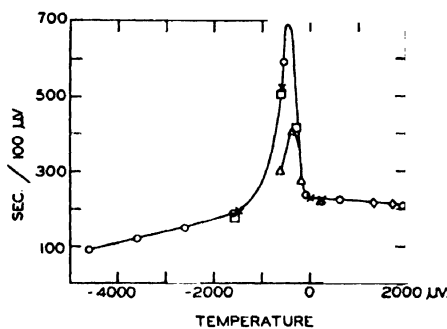


FIG. 7

FIG. 6. Observed heating times for gel nearly saturated with benzene.^{2,3} X, experiment 21, cooled to liquid air temperature; O, experiment 22, cooled to liquid air temperature slowly, between $\pm 3.5^\circ\text{C}$. for 48 hr., at carbon dioxide temperature for 18 hr.; □, experiment 23, cooled to carbon dioxide temperature; Δ, experiment 24, cooled to carbon dioxide temperature.

FIG. 7. Observed heating times for gel nearly saturated with water.² O, experiment 44, cooled to liquid air temperature; X, experiment 45, cooled to carbon dioxide temperature; □, experiment 48, cooled to carbon dioxide temperature, experiment interrupted at -780 microvolts and held between -780 and -730 microvolts for 3.5 hr.; Δ, experiment 46, cooled to -20°C .; ◇, experiment 47, started from room temperature.

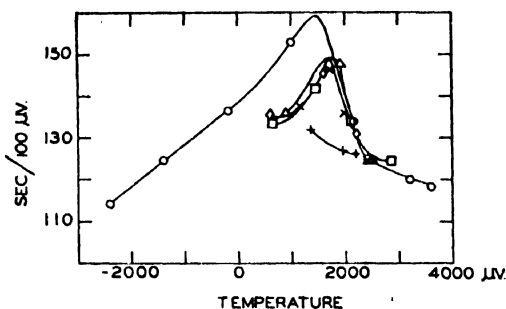


FIG. 8

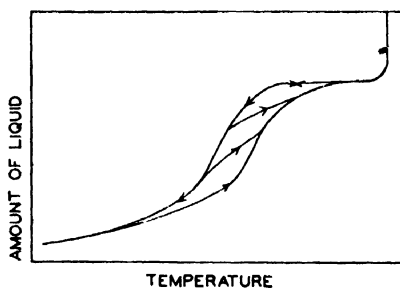


FIG. 9

FIG. 8. Observed heating times for gel nearly saturated with naphthalene.³ O, experiment 37, cooled to -89°C .; Δ, experiment 42, cooled to 2.5°C . rapidly; □, experiment 39, cooled to 5°C . slowly; ◇, experiment 40, cooled to 5°C .; X, experiment 43, cooled to 5°C . then heated to 15°C . at 2.5 times the usual rate, before taking readings; +, experiment 38, started at room temperature.

FIG. 9. Hypothetical curve, showing hysteresis in amount of liquid in gel

¹ In order to simplify the curves only every fifth point and the last point were plotted.

² The differences in experiments 21, 22, and 23 at the high-temperature end of the curves were due to different rates of evaporation of benzene from the calorimeter, which was not sealed vapor-tight. Because of previous loss, the vapor pressure of benzene was less in the following run.

which represent the amount melting per degree rise in temperature, are similar to the curves in figures 7 and 8. This is the same as the hysteresis in adsorption and desorption measurements with the amount of melt corresponding to the amount adsorbed.

Figure 10 shows typical curves obtained with different concentrations of sorbate. The high values at the low-temperature end of the curves are the result of a complication. The lid of the calorimeter did not seal on tight, and, during cooling, oxygen from between the cylinders was adsorbed on the gel in some experiments. During the measurements the heat of desorption caused these high values. It is apparent that this effect

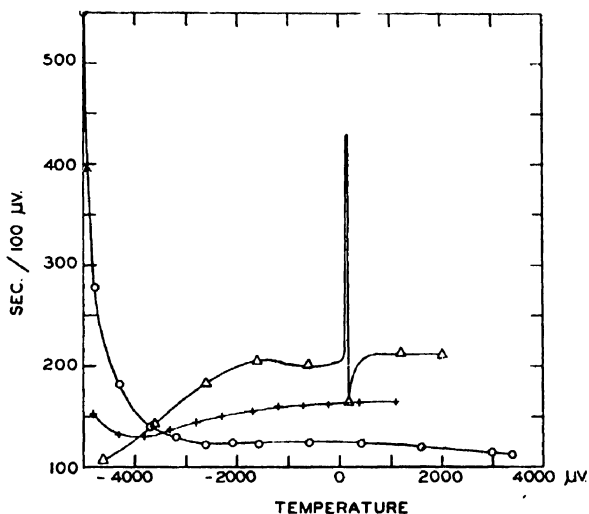


FIG. 10. Observed heating times for silica gel with various amounts of benzene, showing desorption of oxygen.² O, experiment 14, activated gel; +, experiment 16, gel with 31 per cent benzene; Δ , experiment 19, gel saturated with benzene and some excess.

diminishes with increasing concentration of sorbate and is absent with saturated gels.

TREATMENT OF OBSERVATIONS

The heat capacities were calculated from the times of heating. The heat capacity of the sorbate was obtained by subtracting from the heat capacity of the gel and sorbate that of the gel present.

The heat capacity of activated silica gel, as measured in experiment 14, is given in the third column of table 2. However, because of the desorption of oxygen, only those values above 0°C. were used in the calculations of the heat capacity of the sorbate. Below 0°C. estimated values, shown in the last column, were used instead. These were the sum of the heat

capacity of silica as measured in this apparatus and that of 3.25 per cent ice as given in the International Critical Tables. The heat capacity of silica was the average of two runs (Nos. 9 and 10, table 2) with 167 g. and 205 g. of Merck's C.P. sea sand. The average difference between 9 and 10 was 0.85 per cent, and their mean averages were 3.3 per cent higher than the values of Simon (4).

Values for the difference in the heat capacity of the sorbate in its adsorbed and normal state are recorded in table 3 and some are shown in figure 11.⁴ The values are for the amount of sorbate associated with 100 g. of activated gel, rather than per gram of sorbate, in order that the con-

TABLE 2
Specific heats used in calculations
Values are given in calories per degree per 100 grams

TEMPERATURE	HEAT CAPACITY OF SILICA	HEAT CAPACITY OF ACTIVATED SILICA GEL	
	Average of runs 9 and 10	As measured in experiment 14	Estimated
°C.			
126	5.45	48.6	8.8
147	6.08	30.2	10.7
167	6.82	23.0	12.0
184	7.47	20.1	13.1
201	8.01	18.4	14.1
217	8.44	17.8	14.8
232	8.92	17.5	15.7
246	9.38	17.3	16.6
260	9.83	18.2	17.4
273	10.27	18.9	18.3
286	10.65	19.2	
299	11.00	19.8	
311	11.28	20.1	
323	11.56	20.5	
334	11.80	20.8	
346	12.03	21.3	

tributions of the various portions of the sorbate under different capillary forces may be additive instead of averaged, and that the results may be independent of the amount of excess sorbate which has normal heat capacity.

Table 3 shows that at temperatures below its normal melting point the heat capacity of the sorbate is in excess of its normal heat capacity. If the sorbate is condensed in capillaries in the gel, then the difference is accounted for as follows: (1) by the heat of fusion of sorbate melting at

⁴ See also figures 3 to 6 of the second paper on this subject (J. Phys. Chem. **42**, 381 (1938)).

lower temperatures; (2) by the heat of wetting of the gel by the melt; (3) by the heat of compression due to diminishing surface forces; and (4) by the difference between the specific heat of the melt and that of the normal solid. The difference increases with rising temperature to a maximum below the normal melting point. At this temperature presumably most of the sorbate is now melted. At the normal melting point the heat of fusion of only the excess sorbate is observed.

These values are given in the last row (opposite "n.m.p."). Above the normal melting point, the differences are small. They are partly due to vaporization of the sorbate from the calorimeter, which absorbs heat. Such loss also makes the estimate of the amount of sorbate in ensuing runs

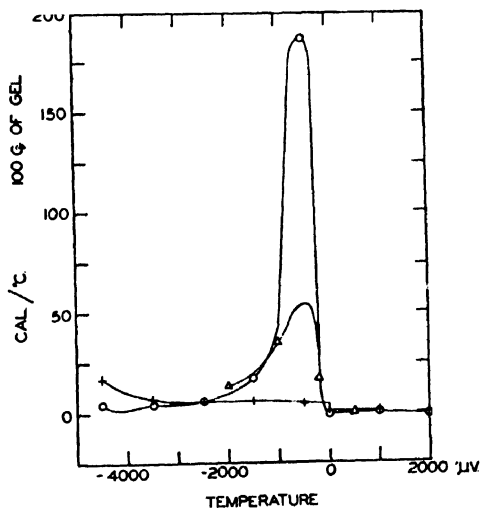


FIG. 11. Heat capacity of adsorbed water in excess of normal heat capacity of water. +, experiment 36, gel 7.1 per cent saturated; Δ , experiment 51, gel 37.4 per cent saturated; O, experiment 44, gel 91.4 per cent saturated.

too high. For this reason the results for benzene are not in as good agreement as those for the less volatile sorbates. It is to be noted that these differences are especially small in comparison with the total measured heat capacity of the systems, which, for example, for experiment 44 at 286°K., is 70.2 cal. per degree.

Figure 11 indicates how the results depend upon the composition of the gel-sorbate system. In experiment 36 the gel was 7 per cent saturated with water. Since the surface forces on this small amount of sorbate would be large, it would be expected to be liquid over most of the interval shown. The result then would be the difference in heat capacity of super-cooled water and ice. At low temperatures the values are high because of the desorption of oxygen. The results for the 37 per cent saturated

TABLE 3
Heat capacity of substances on silica gel less their normal heat capacity

Experiment..... Moles per 100 g. of gel.....	BENZENE				WATER				NAPHTHALENE		P-NITRO- TOLUENE*
	17	21	19	36	51	44	45	48	50	52	
	0.542	0.544	0.618	0.217	1.145	2.8	2.8	2.8	0.367	0.378	
*K.	CALORIES PER DEGREE PER AMOUNT OF SORBATE ASSOCIATED WITH 100 G. OF ACTIVATED GEL										
126	4.3			17.1		3.7					2.8
147	2.6	2.9	2.8	9.2		2.1					1.3
167	3.7	2.6	1.6	7.1		3.7					2.0
184	4.5	3.3	2.8	5.8		5.1					1.6
201	5.5	4.4	4.0	5.4		6.5					1.4
217	5.6	4.5	5.0	5.0	13.0	9.2			4.8	4.0	1.4
232	4.7	3.5	5.4	5.7	19.3	16.5	15.7	16.0	3.6	3.4	1.4
246	2.7	1.2	4.6	4.6	35.5	42.9	41.1	41.5	3.5	3.4	1.5
260	1.5	0.3	2.0	4.5	54.2	185.8	160.1	174.4	4.1	3.9	2.6
268			2.5	4.2	17.0	43.5	30.8	38.0			4.5
273	0.9	-0.2	0.2	0.7†	0.7†	-0.8†	-1.3†	-5.9†	5.6	5.1	7.1
281											9.5
286	-0.3	-2.3		0.8	0.2	-0.3	-2.6	-5.7	7.6	7.4	9.3
299	-1.0	-2.4	-0.3	1.3	0.1	-0.4			11.5	11.4	3.4
311	1.4	0.5	1.2			-0.6			16.0	15.9	2.7
323	3.7	1.8	1.7			-0.9			10.4	12.3	16.4
334									0.4	1.4	
346										-1.4	
n.m.p.§	-1283	-1290	-1350†	-312	-1645	-4022	-4022	-4022	-1648	-1700†	

* Normal specific heat (estimated as the mean molecular specific heat of *p*-dinitrobenzene and *p*-xylene) = 12.60 + 0.09917 cal. per mole degree.

† Excess sorbate melting. These differences indicate gel capacity to be 0.57 mole of benzene in experiment 19, 3.02 moles of water in experiment 35, 3.11 moles of water in experiment 49, and 0.378 mole of naphthalene in experiment 52.

‡ Heat capacity of sorbate less specific heat of liquid water.

§ Normal melting point.

gel are close to those for the 92 per cent saturated gel for an interval, but reach a maximum at a temperature 3°C. lower. Other experiments shown in table 3 indicate that the results are independent of any excess sorbate present. Because of the presence of this frozen excess sorbate, it is unlikely that the remaining sorbate could have supercooled.

CONCLUSION

Substances adsorbed on silica gel melt at temperatures below those at which they would melt in their normal state. Fusion begins at a very low temperature, but the melting temperature rises as increasing amount of melt is formed on the gel. Also, the amount melting increases with the temperature until nearly all the sorbate has melted. In the case of saturated gels this maximum melting occurs with benzene 44°C. below its normal melting point, with water 12°C. below, with naphthalene 40°C. below, and with *p*-nitrotoluene 41°C. below. The amount melting per degree is a reproducible function of the temperature, independent of the rate of cooling or heating, provided the experiments start from the same low temperature. Otherwise there is hysteresis, wherein the amount of solid phase at a given temperature is greater in the experiment starting at the lower temperature.

This is all in accord with the expected behavior of substances condensed in fine capillaries. The negative pressure on the condensed liquid, resulting from surface forces, reduces the escaping tendency of this phase, and a lower temperature is necessary for equilibrium with a solid phase not acted on by surface forces.

SUMMARY

1. The Andrews calibrated heat conduction method was used to measure the heat capacity of substances adsorbed on silica gel. Water, naphthalene, benzene, and *p*-nitrotoluene were investigated in various concentrations.

2. Results from typical experiments for the difference in heat capacity of the adsorbed and normal states of the amount of sorbate associated with 100 g. of activated gel were tabulated. Expressed in this manner, the results were independent of the amount of excess sorbate and over a limited temperature range were independent of concentration for unsaturated gels.

3. Only material in excess of that which saturates the gel melts at its normal melting point. Melting of the adsorbed phase is indicated at lower temperatures by its abnormally large heat capacity. This increment is largest at -12°C. with water, and with the other sorbates at temperatures about 40°C. lower than their normal melting points.

4. These heat capacities were quite reproducible and independent of

the rate of cooling or heating, if started from the same lowest temperature. If previously cooled to a lower temperature, the system had greater heat capacity over certain temperature intervals.

5. The heat of desorption of oxygen was apparent in some experiments. On pure silica gel it was observed up to 240°K. But the larger the amount of sorbate on the gel, the smaller was the capacity of the gel for oxygen.

6. The lowered melting points of the substances adsorbed on silica gel are in agreement with the theory that they are condensed in the capillary voids of the gel and that the forces arising from the highly concave surface of the liquid sorbate are responsible for the lowered escaping tendency of this phase.

We are much indebted to Dr. D. H. Andrews for the apparatus and technique which he has developed and made available for these experiments. Also we wish to acknowledge the generous assistance of Dr. S. Goldheim and Dr. V. Deitz in the laboratory, and of Dr. N. Hackerman in the preparation of this report.

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THE EFFECT OF SURFACE FORCES ON MELTING¹

W. A. PATRICK AND W. A. KEMPER

Department of Chemistry, The Johns Hopkins University, Baltimore, Maryland

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The preceding paper (5) described calorimetric observations from which the lowered melting temperatures of certain substances adsorbed on silica gel were inferred. In this paper calculations are made of the melting temperatures to be expected if capillary condensation is the cause of adsorption, and the calculations are compared with the calorimetric observations of the preceding paper.

MELTING TEMPERATURES OF ADSORBED SUBSTANCES

It is well known (1) that certain adsorbents are supposed to have capillaries in which vapors condense to liquids, and that the vapor pressure of the condensate increases as the capillaries fill and the stress arising from surface forces decreases. The temperature at which this condensate will freeze depends upon how the solid forms. There are several conceivable ways in which the solid might form, each affecting the stresses on the two phases and consequently the freezing temperature, differently. The solid may form on the walls, narrowing the capillaries. It may form entirely within the body of the liquid, causing but little change in the surface of the liquid. Or, it may form by a process of evaporation and sublimation entirely outside the liquid. In this case the vapor pressure of the liquid remaining would be that of the same amount of liquid with no solid present. The stresses on the solid formed would also be different in these cases. In the last case, the vapor pressure of the small solid particles might be increased by a surface tension of the solid, if such a force exists.

It will here be assumed that: (1) *the stress on the unfrozen sorbate is independent of the amount of frozen sorbate present,*² and (2) *the frozen sorbate is not under any stress from surface forces.* The melting temperature will then be calculated as the temperature at which adsorbed liquid and normal solid have the same vapor pressure.

¹ This article is based on a dissertation submitted by W. A. Kemper to the Board of University Studies of the Johns Hopkins University in partial fulfillment of the requirements for the degree of Doctor of Philosophy, June, 1934.

² In this paper the assumptions made are printed in italics.

The vapor pressure of the adsorbed liquid, p , is estimated by the Patrick isotherm (6)

$$X_l v_l = k \left(\frac{p\sigma}{\bar{p}} \right)^n \quad (a)$$

In this, in accord with assumption 1, X_l , the amount of melt on the gel, is used in place of the total amount of sorbate, customarily used in the equation at temperatures above the melting point of the sorbate. v_l , σ , and \bar{p} are the specific volume, the surface tension, and the normal vapor pressure of liquid sorbate at the temperature concerned. The subscript l denotes a property of the liquid state and the overrule ($\bar{}$) refers to the value for the unadsorbed or normal state. k and n are constants which characterize the adsorbent. This equation with the same values of k and n gives the vapor pressure isotherm at any temperature and, with the exception of water, for any sorbate.

The normal vapor pressure of liquid, \bar{p} , at temperature T , in terms of its value \bar{p}_m at the normal melting point, is given by the Clapeyron equation

$$\ln \frac{\bar{p}}{\bar{p}_m} = \int_{T_m}^T \frac{H_g - H_l}{RT^2} dT$$

where H_g and H_l are the heat content of vapor and liquid and R is the gas constant.

With this value of \bar{p} , equation a becomes

$$\ln \frac{p}{\bar{p}_m} = \frac{1}{n} \ln \frac{X_l v_l}{k\sigma^n} + \int_{T_m}^T \frac{H_g - H_l}{RT^2} dT \quad (b)$$

The vapor pressure of solid at the temperature T , in terms of its value at the normal melting point, T_m , also \bar{p}_m , is

$$\ln \frac{\bar{p}_s}{\bar{p}_m} = \int_{T_m}^T \frac{H_g - H_s}{RT^2} dT \quad (c)$$

Equating p and p_s from equations b and c, one obtains the melting temperature, T , corresponding to the amount of melt, X_l :

$$\frac{1}{n} \ln \frac{X_l v_l}{k\sigma^n} = \int_{T_m}^T \frac{H_l - H_s}{RT^2} dT$$

or

$$\frac{R}{n} \ln \frac{X_l v_l}{k\sigma^n} = \frac{\bar{H}_f}{T_m} - \frac{\bar{H}_f}{T} + \int_{T_m}^T \frac{1}{T^2} \int_{T_m}^T (C_{pl} - C_{ps}) dT^2 \quad (d)$$

where C_{pl} and C_{ps} are the specific heats of liquid and solid sorbate and H_f is the heat of fusion at the normal melting point.

An approximate equation, which neglects the change in the heat of fusion with temperature, is

$$\frac{RT}{nH_f} \ln \frac{X_l v_l}{k\sigma^n} = \frac{T - T_m}{T_m} \quad (d')$$

With these equations (d or d'), when k and n are known for the adsorbent, one can calculate X_l , the amount of sorbate that can exist as liquid at temperature T . Any sorbate in excess of this is solid. This temperature is termed the melting temperature corresponding to the amount of melted sorbate, X_l .

Calculations of this function, X_l , were made for the four compounds studied in the preceding paper (5). The values of k and n were those which best fitted a set of adsorption isotherms for benzene and water which were obtained in the laboratories of the Silica Gel Corporation on a gel of the same type as ours (7). The similarity of the two gels was verified by comparing their water content when activated, a definite characteristic of a gel. Our activated gel contained 0.0325 g. of water per gram of silica as compared to 0.0324 g. of water per gram of silica reported for the gel from which the adsorption data were obtained.

The following are the resulting values:

$$\log X_l v_l = 1.13 + 0.46 \log \frac{p\sigma}{\bar{p}}$$

for organic sorbates, and

$$\log X_l v_l = -0.145 + 1.05 \log \frac{p\sigma}{\bar{p}}$$

for water where X_l is grams of water (above 3.24 per cent) per 100 grams of activated gel.

The specific heat of *p*-nitrotoluene, which has not been reported, was estimated as the mean of the molar specific heats of *p*-xylene and *p*-dinitrobenzene. The values obtained were $C_{ps} = 12.6 + 0.0991T$ and $C_{pl} = 21.17 + 0.085T$ cal. per °C. mole.

The other data for the calculations were obtained from accredited sources.

The actual values of X_l were not calculated from the observations in the previous report. However, the values of X_l , calculated from equation d, are shown in figure 1. Since the amount melting increases with temperature until melting is complete, the observed temperature of maximum melting can be compared with calculations of the temperature at which the sorbate would be completely melted. The temperature at which the

heat capacity was a maximum was taken as the temperature of maximum melting. Values of X_l equal to the total amount of sorbate present in these experiments are indicated on the curves by the horizontal lines. A comparison of these two is given in table 1.

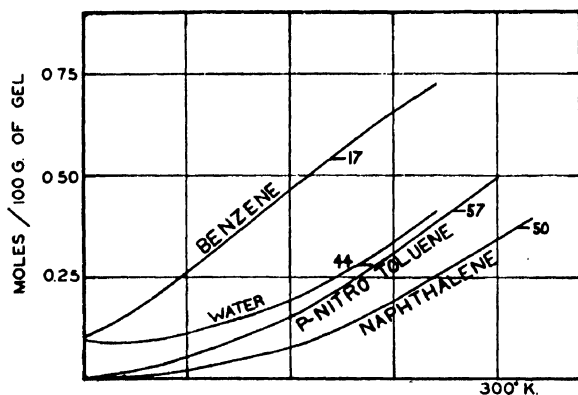


FIG. 1. Calculated amount of unfrozen sorbate. Numbered horizontal line indicates total sorbate present in the experiment indicated

TABLE 1

Comparison of observed temperature of maximum melting with calculated temperature at which the sorbate would be completely melted

SUBSTANCE	EXPERIMENT NO.	CALCULATED TEMPERATURE AT WHICH MELTING IS COMPLETE	OBSERVED TEMPERATURE OF MAXIMUM HEAT CAPACITY
		°K.	°K.
Benzene.....	17	219	229
Water.....	44	231	260
Naphthalene.....	50	307	313
p-Nitrotoluene.....	57	278	283

The observed temperatures are not as low as the calculated values. The discrepancy is believed to be due to a hysteresis. The difference is largest in the case of water, and water is known to show more hysteresis than other sorbates.

CALCULATIONS OF THE APPARENT HEAT CAPACITY OF THE ADSORBED PHASE

In the previous paper (5) values were obtained for the difference in apparent heat capacity of the adsorbed phase and normal solid sorbate. If the theory of capillarity is correct, this difference consists of the following terms:

(1) $(C_{pl} - C_{ps})X_l$, the difference in heat capacity of adsorbed liquid and normal solid times the amount of adsorbed liquid.

(2) $(H_l - H_s) \frac{dX_l}{dT}$, the heat of fusion times the amount of melting per degree increase in temperature.

(3) $X_l \left(\frac{\partial H_l}{\partial P} \right) \frac{dP_l}{dT}$, the heat of compression for the change in pressure accompanying one degree rise in temperature.

(4) $-H_\omega \frac{d\omega}{dT}$, minus the heat of wetting per unit area times the amount of surface newly wetted by melt per degree rise in temperature.

(5) $\omega \frac{dH_\omega}{dT}$, the heat capacity of the surface layer.

The evaluation of each of these terms for the amount of sorbate contained on 100 g. of silica gel follows. In the calculations the *change in density of adsorbed liquid with pressure will be neglected*.

The heat capacity of a liquid is independent of pressure, if *thermal expansion is assumed to be linear*. For

$$\frac{\partial C_{pl}}{\partial P} = T \frac{\partial^2 v_l}{\partial T^2} = 0$$

Hence the first term is

$$(\bar{C}_{pl} - \bar{C}_{ps}) X_l \quad (1)$$

The amount melting per degree is obtained from the derivative of equation d with respect to temperature, σ being represented by $A + BT$ and $\frac{1}{v_l} \frac{\partial v_l}{\partial T}$ by E , the coefficient of cubical expansion. The expression is

$$\frac{dX_l}{dT} = \frac{nX_l}{RT^2} \left[\bar{H}_f + \int_{T_m}^T (C_{pl} - C_{ps}) dT + \frac{BRT^2}{A + BT} \right] - EX_l \quad (e)$$

The heat of fusion is

$$H_l - H_s = \bar{H}_f + \int_{T_m}^T (C_{pl} - C_{ps}) dT + \int_0^{P_l} \left(\frac{\partial H_l}{\partial P} \right)_T dP_l$$

where P_l is the hydrostatic pressure on the adsorbed liquid.

The value of the last term, the heat of expansion, is obtained from the equation of state:

$$\left(\frac{\partial H_l}{\partial P} \right)_T = v_l - T \left(\frac{\partial v_l}{\partial T} \right)_P$$

The second term of this is neglected so that

$$\int_0^{P_l} \left(\frac{\partial H_l}{\partial P} \right)_T dP_l = v_l P_l$$

In order to change from the auxiliary function P_l to T the following procedure can be used: P_l is related to the vapor pressure of the liquid by the equation for the vapor pressure of a liquid under hydrostatic pressure,

$$RT \ln p/\bar{p} = v_l P_l$$

Then, using the value of p/\bar{p} from equation a, one obtains

$$v_l P_l = \frac{RT}{n} \ln \frac{X_l v_l}{k\sigma^n}$$

Finally by means of equation d the value of $v_l P_l$ is found in terms of T .

$$v_l P_l = \frac{\bar{H}_f T}{T_m} - \bar{H}_f + T \int_{T_m}^T \frac{1}{T^2} \int_{T_m}^T (C_{pl} - C_{ps}) dT^2 \quad (f)$$

This is a fundamental equation and also could have been obtained from

$$v_l dP_l = \frac{H_l - H_s}{T} dT$$

which results from equating

$$dF_l = dF_s$$

where F denotes free energy.

Using equation f, and simplifying, one then obtains for the heat of fusion,

$$H_l - H_s = \frac{\bar{H}_f T}{T_m} + T \int_{T_m}^T \frac{C_{pl} - C_{ps}}{T} dT \quad (g)$$

The second term of the heat capacity, $(H_l - H_s) \frac{dX_l}{dT}$, can now be obtained by multiplying equations e and g.

As the amount of liquid is increased by melting, the negative pressure decreases and the liquid is subject to compression. The increase of pressure on the liquid with temperature is found by taking the derivative of equation f with respect to temperature. When v_l is represented by $v_l = v_{l_0} (1 + E\Delta T)$, the equation of state becomes

$$\left(\frac{\partial H_l}{\partial P} \right)_T = \frac{1 + ET_0}{1 + E\Delta T} v_l$$

(This coefficient of v_l is small and was neglected above in calculating the correction to the heat of fusion for the expansion of newly melted liquid.) The heat of compression is then

$$X_l \frac{dP_l}{dT} \left(\frac{\partial H_l}{\partial P} \right)_T = X_l \frac{1 - ET_0}{1 + E\Delta T} \left[\left(\frac{\bar{H}_f}{T_m} - \frac{\bar{H}_f}{T} + \int_{T_m}^T \frac{1}{T^2} \int_{T_m}^T (C_{pl} - C_{ps}) dT^2 \right) \left(\frac{1 - ET_0}{1 + E\Delta T} \right) + \frac{\bar{H}_f}{T} + \frac{1}{T} \int_{T_m}^T (C_{pl} - C_{ps}) dT \right] \quad (3)$$

The heat content per unit area of surface,

$$H_\omega = \sigma - T \frac{d\sigma}{dT} = A$$

where A was defined by $\sigma = A + BT$.

Activated silica gel is assumed to be covered with a monomolecular film of water. As melted sorbate fills the capillaries, this water-air interface is replaced by a water-sorbate interface. The heat evolved will be the heat content of the water-air interface less that of the water-sorbate interface. By Antonow's rule (2), which is valid if the molecules of the second liquid are not oriented at the water interface, this difference is equal to the heat content of the sorbate-air interface, which is A times the area.

The change in area of surface, ω , is calculated by considering a differential element of the capillary as a cylinder. The element of volume is $\pi r^2 dh$ and the element of area is $2\pi r dh$. Hence

$$\frac{d\omega}{v_l dX_l} = \frac{2}{r}$$

and since

$$P_l = -\frac{2\sigma}{r}$$

$$\frac{d\omega}{dT} = -\frac{v_l P_l}{\sigma} \frac{dX_l}{dT}$$

Using the value of $v_l p_l$ from equation f, one obtains for the fourth term,

$$H_\omega \frac{d\omega}{dT} = \frac{AT}{A + BT} \left[\frac{\bar{H}_f}{T_m} - \frac{\bar{H}_f}{T} + \int_{T_m}^T (C_{pl} - C_{ps}) dT^2 \right] \frac{dX_l}{dT} \quad (4)$$

Since the heat content of the surface,

$$H_\omega = \sigma - T \frac{d\sigma}{dT} = A$$

and A is independent of the temperature,

$$\omega \frac{dH_\omega}{dT} = 0 \quad (5)$$

The sum of the above five terms represents, on the basis of the assumptions that have been made, the apparent heat capacity of the adsorbed substance in excess of its heat capacity in its normal solid state, if capillarity is the cause of its adsorption.

Calculation of all of these quantities for the four substances reported in

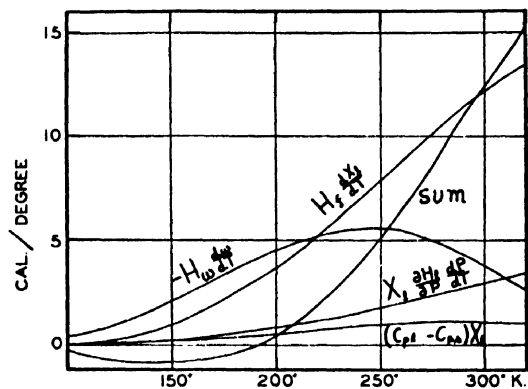


FIG. 2. Calculated component parts of extra heat capacity of naphthalene associated with 100 g. of activated gel

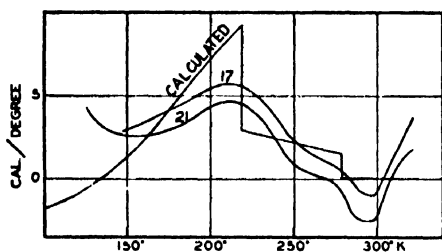


FIG. 3

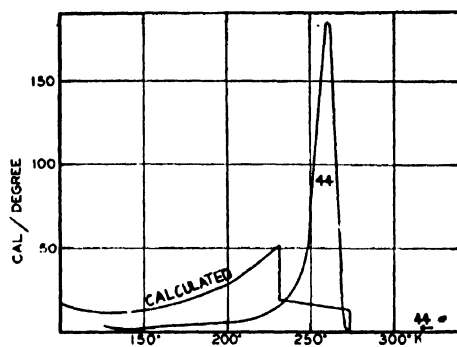


FIG. 4

FIG. 3. Additional heat capacity of benzene adsorbed on 100 g. of gel

FIG. 4. Additional heat capacity of water adsorbed on 100 g. of gel

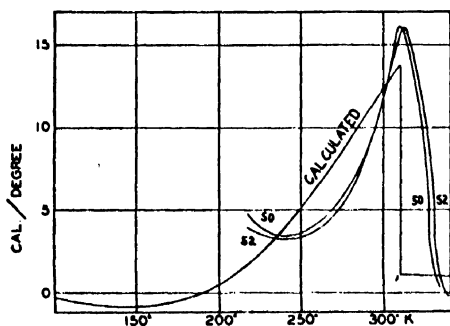


FIG. 5

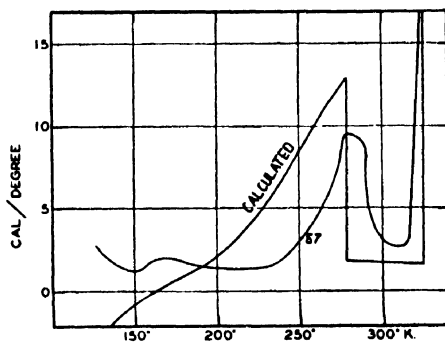


FIG. 6

FIG. 5. Additional heat capacity of naphthalene adsorbed on 100 g. of gel

FIG. 6. Additional heat capacity of *p*-nitrotoluene adsorbed on 100 g. of gel

the previous paper has been made. Figure 2 shows the calculated increase in heat capacity of adsorbed naphthalene and the components from which it was evaluated. Figures 3 to 6 show the calculated and observed values for the increase in heat capacity of benzene, water, naphthalene, and *p*-nitrotoluene when adsorbed on the gel.

The observed values lie on the high temperature side of the calculated values, and once more the poorest agreement found is in the case of water. The hysteresis would cause the values observed on heating to lag behind those calculated for equilibrium conditions.

DISCUSSION

One might suppose that the small size of the solid particles would have some effect on the melting point. Meissner (4) observed a melting-point lowering of a fraction of a degree with crystals 0.8μ thick. However, Meissner's experiments and most of the theoretical treatments have been concerned with a situation in which the particles were within the melt. In the present experiments the simplifying assumption has been made that the solid has normal vapor pressure. Kubelka (3), who discussed various theoretical equations, proposed a similar simplification for sorbates in silica gel or charcoal. He derived an approximate equation for the melting-point lowering as a function of the radius of the capillaries, in which he assumes that the heat of fusion is constant with the temperature.

In this paper we have calculated the temperature at which normal solid is in equilibrium with an adsorbed phase, which follows the Patrick isotherm modified for a supercooled liquid. It is, of course, possible that the use of some other isotherm equation based upon some other theory of adsorption might give equally good results. However, the assumptions made contain intrinsically a good deal of the idea of capillarity. To this extent, accordingly, such agreement as exists between the calculations of the present paper and the calorimetric observations lends some support to the theory of capillary condensation. A closer agreement could not be expected without eliminating the hysteresis phenomenon.

SUMMARY

1. The Patrick equation for adsorption was extended below the normal melting point of the sorbate by using as values for normal vapor pressure, surface tension, and specific volume, those of supercooled liquid sorbate.
2. A general equation was obtained for the melting temperature of substances condensed in porous adsorbents.
3. Calculations were made of the melting temperatures of the four substances adsorbed on silica gel reported in the previous paper (5). The calculations used only two constants characterizing the gel, k and n of the Patrick equation. The values employed for these were obtained from

a study of adsorption isotherms of benzene and water on this gel at higher temperatures. The temperatures at which the last portions of the sorbates were calculated to have melted averaged only 14°C. lower than the temperatures at which the maxima in the heat capacities of the systems had been observed. It is believed that the calculated temperatures are lower because of hysteresis.

4. Further equations were derived from the various terms which compose the difference between heat capacity of the sorbate in the adsorbed state and in its normal solid state.

5. The results of these calculations were compared with the observations reported in the previous paper (5).

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ELECTROKINETIC ASPECTS OF SURFACE CHEMISTRY. IV

THE RATIO OF ELECTROÖSMOSIS TO ELECTROPHORESIS

LAURENCE S. MOYER¹

*Department of Botany, University of Minnesota, Minneapolis, Minnesota, and the
Biological Laboratory, Cold Spring Harbor, New York*

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Abramson (1), Daniel (6), Dummett and Bowden (7), and Bull (5) have found that the electrophoretic mobility, v , of inert particles coated with protein is the same as the electroösmotic mobility, u , of the solution past the wall of the electrophoresis cell when it, too, is coated with the same protein. White, Monaghan, and Urban (15, 16) have agreed that the ratio R (where $R = u/v$) is equal to unity in the presence of salts when a concentration of gelatin of about 0.01 per cent or more is present, but they contend that in the absence of added salt R assumes values between 2 and 2.3. Moyer and Abramson (13) investigated this reported value of R , using concentrations of gelatin down to 0.02 per cent at specific conductances of about 4×10^{-6} ohm⁻¹-cm.⁻¹, yet were unable to detect a significant rise of the ratio from unity. Recently, however, White and Fourt (14) have again reported divergent ratios and maintain that the difference between the results of Moyer and Abramson and those of White, Monaghan, and Urban, in the absence of added salt, is due to the higher gelatin concentration used by Moyer and Abramson. It was claimed that, although the coating was complete in all concentrations of gelatin employed, the effect of "an increase in gelatin concentration, as of increasing electrolyte concentration, is to bring the ratio to unity".

As proof of complete coating of the cell and particles, the identity of their isoelectric points was presented. Abramson (2) has pointed out that identity of isoelectric points is a necessary but not a sufficient condition to establish identity of surfaces. (See in particular experiments performed by the writer (10) with aluminum oxide particles coated with egg albumin.) For their experiments Abramson and Moyer and Abramson have always been careful to place both the cell and the particles in strong (1 per cent) gelatin solutions until coating is established, and then to dilute the solutions to the gelatin concentration desired, using this device in order to have a *low* conductance with a *complete* film.

¹ John D. Jones Scholar at the Biological Laboratory, Cold Spring Harbor, New York, during the summer of 1937.

On the other hand, White *et al.* have contended that merely placing wall and particles in contact with 0.01 per cent gelatin solutions is sufficient to coat the surfaces completely and that the high values for the ratio are due to other causes. Willey and Hazel (17) have recently investigated the problem, using particles of colloidal ferric oxide in gelatin solutions. By exposing the particles and cell walls to dilute gelatin solutions, they concluded that to get identical surfaces, other than at the isoelectric point and in the absence of added salts, about 0.2 per cent gelatin was required. Below this concentration divergent values for u and v were reported. Addition of salts brought the ratio to $R = 1.0$. Further details are presented in their paper. Similar results have been reported by van Gils (8) who states, however, that complete coating is attained first at a concentration of 0.05 per cent gelatin in the absence of salts.

In the experiments now to be presented, quartz particles were placed in 1 per cent solutions of electrodyalyzed "Silver Label" gelatin (manufactured by the American Carbon Works) for fifteen minutes. They were then centrifuged and the supernatant liquid removed. Some of the sediment was diluted to 0.001 per cent nominal concentration of gelatin. Meanwhile an Abramson horizontal microelectrophoresis cell (a modification of a cell described by Northrop and Kunitz but constructed of one piece of glass)² (2, 9) was also filled with some of the original gelatin solution. After the lapse of time, the excess gelatin was removed from the cell by repeated rinsing (at least four times) with distilled water. Precaution was taken to coat the walls of all measuring vessels with gelatin in the same way. The suspension was then introduced into the cell and measurements performed by our usual methods (9, 13).

Figure 1 shows the observed mobility, V , of these particles at various depths, X , from the top of the cell. The specific conductances of these solutions of 0.001 per cent gelatin were about 4×10^{-6} ohm⁻¹cm⁻¹. The smooth, unbroken curve has been drawn from the usual parabolic equation (13), assuming $R = 1.0$. The two upper curves (dashed) have been calculated, taking $R = 1.5$ and $R = 2.0$. Other experiments in which Pyrex glass was used instead of quartz gave the same results. Under our conditions, it seems that the ratio is very near unity.

These experiments indicate that once the surfaces are coated, they retain their coating even after great dilution of the gelatin. It appears probable that the exposure of particles to initially dilute gelatin solutions in distilled water may not produce a complete, uniform film. The ratio of unity hardly permits one to draw conclusions (17) as to the value of the constant

² This cell has a rectangular cross section, with non-polarizable electrodes, and has been shown to yield data which check quantitatively with results obtained from measurements in U-tubes (3, 4, 9). White *et al.* and Willey and Hazel used cells for which, as yet, no comparisons of this character seem to have been presented.

of proportionality in the Helmholtz-Smoluchowski equations of electroosmosis and electrophoresis, except that it is the same in both equations when the coated surfaces of the particle and the wall are exposed to identical conditions. The agreement between mobilities of certain dissolved and adsorbed proteins suggests that these adsorbed proteins confer their

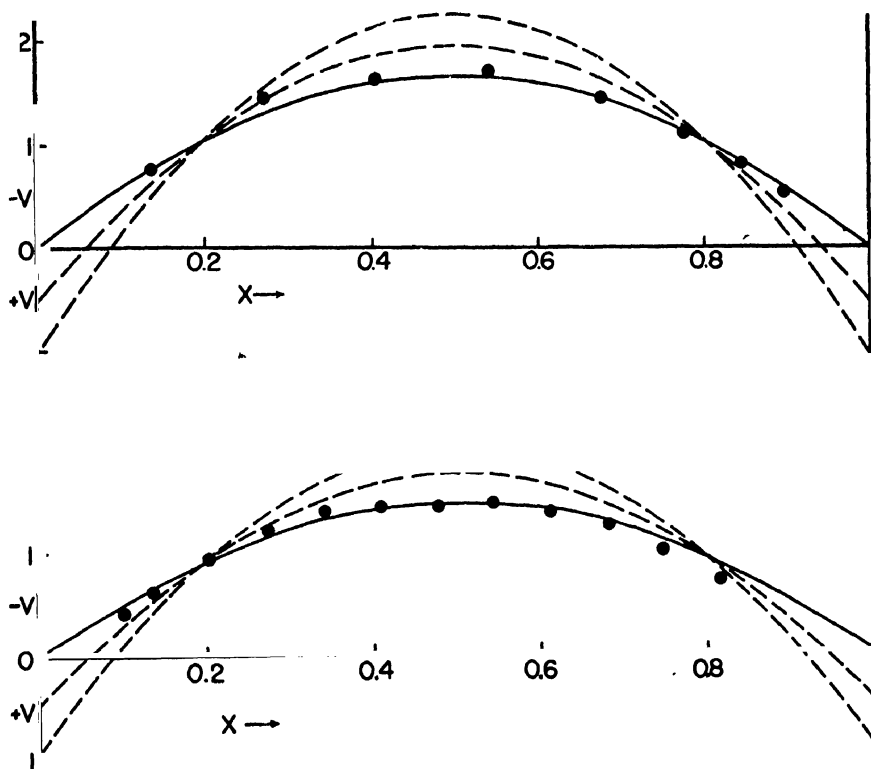


FIG. 1. The mobility, V , of gelatin-coated particles at various levels, x , of a microelectrophoresis cell. Both experiments were performed at a final gelatin concentration of 1:100,000 without added salt, and at a specific conductance of about $4 \times 10^{-6} \text{ ohm}^{-1}\text{-cm}^{-1}$. The smooth, unbroken curve (lowest) has been calculated, assuming $R = 1.0$. The two upper curves (dashed) have been calculated, taking $R = 1.5$ and $R = 2.0$. It is evident that, within the limits of error, the experimental points fit the curve for $R = 1.0$, indicating that electrophoresis and electroösmosis are equal. The mobilities given in each figure have been reduced to unit field strength.

own effective radii on the particle and the wall surfaces (2, 11, 13). Hence the constant might assume varying values, depending on the ionic strength and effective radius (12), yet under any given conditions the proportionality constant would be the same for both wall and particle, when completely coated, and the ratio would remain at $R = 1.0$. Gelatin is

a protein of non-uniform particle size. In certain cases this might hinder the attainment of identity of surfaces (by adsorption of slightly different components by wall and particle), yet for systems where $R = 1.0$ the surfaces under comparison have probably adsorbed the same component (or mixture of components). Hence under these conditions r would be the mean radius and κr would be statistically the same for both wall and particle.

SUMMARY

The ratio of electroösmotic to electrophoretic mobility of gelatin-coated surfaces is very near unity, even in gelatin solutions as dilute as 0.001 per cent and in the absence of added salt, if care is taken to insure a complete coating.

ADDENDUM

While this paper was in press, White and Fourn published their complete results (J. Phys. Chem. **42**, 29 (1938)). Two of their undialyzed gelatin preparations (Eastman and Coignet) gave high ratios at low concentrations in distilled water *but Agfa gelatin yielded ratios of 1.00, even at 0.01 per cent gelatin in distilled water*. This contradiction to be observed in their own data makes it necessary to scrutinize their experimental method for its precision. White and Fourn report that initial exposure of the wall of the cell to 1 per cent gelatin solutions, and subsequent dilution, failed to reduce the high ratios, but no measurements appear to be presented in which both wall and particles were initially exposed to this concentration, as in our experiments. They mention the ratio of 1.11 obtained by Moyer and Abramson with 0.02 per cent Agfa gelatin in distilled water. That this is not significantly higher than 1.0 is shown by our control experiment (13) in $M/100$ potassium chloride with 0.2 per cent gelatin for which the ratio was 1.07.

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THE DETERMINATION OF MOLAR WEIGHTS OF VAPORS NEAR THE BOILING POINT

J. D. INGLE AND H. P. CADY

Department of Chemistry, University of Kansas, Lawrence, Kansas

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INTRODUCTION

Molecular weights have been determined by a great variety of methods. One of the oldest of these is the determination of the vapor density of the substance and the subsequent calculation of the molecular weight from this. Measurements of vapor density permit not only the calculation of molecular weights, but also the study of heats of vaporization and of the departure of the behavior of the vapor from the perfect gas law.

From a consideration of the perfect gas law it is clear that in order to determine the molecular weight of a vapor it is necessary to know four quantities: namely, mass, volume, temperature, and pressure.

The most famous method, and the one used more than any other for the determination of vapor densities, is that devised by Victor Meyer (4) in 1876. The most important improvements attempted on this method were those of Weiser (6) and MacInnes and Kreiling (3). Other well-known methods of determining vapor densities are those of Lunsen, Gay-Lussac, and Hofmann.

In 1933 Cady devised the most precise and rapid method ever developed for the determination of molar weights from vapor densities. This method is an application of the Westphal balance to vapors. In 1936 Rankin (5) modified Cady's method so that it was possible to determine the vapor densities of substances over a range of temperature, thus enabling one to approach the vapor density of the substance at the boiling point very closely. The apparatus was so constructed that data could be obtained making it possible to correct for any adsorption that might be in evidence as the boiling point of the liquid was approached.

The well-known method of Dumas is often used in measuring vapor densities. Cady proposed the modification of the Dumas method in such a manner as to eliminate the errors possible when weighing a vessel of large surface. The apparatus described in this paper not only eliminates this error but also enables one to determine vapor densities of substances close to their boiling points.

APPARATUS

The apparatus used in measuring the volume and mass of the vapor being studied is shown in figure 1. The volumetric flask F was calibrated after the stopcocks 2 and 3 had been sealed onto the vessel; these two stopcocks were of capillary tubing.

All of the external glass tubing, starting at the distilling flask and ending at the condenser, was wrapped with resistance wire and heated with a current of about 1 ampere while making determinations. This was done to prevent condensation of the vapors in the tubes before they reached the condenser or weighing bottle.

The weighing bottle, not shown in figure 1, was connected at B by a ground-glass joint. The weighing vessel consisted of a tube 10 mm. in

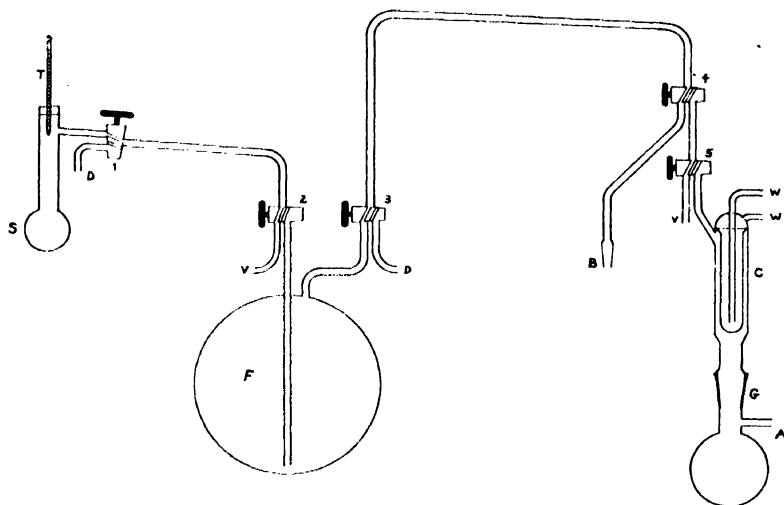


FIG. 1. Apparatus used in measuring the volume and mass of the vapor

diameter and 75 mm. long. Both openings were at the top, one tube extending about 65 mm. down inside the vessel. This tube had a glass-wool plug in a constriction at the lower end. Each of the entry tubes was connected to a small stopcock, one of the stopcocks being sealed to a ground-glass joint so that the weighing vessel could be attached to the main apparatus at B. A counterpoise was used that had the same shape and nearly the same volume as the weighing vessel.

The apparatus used in controlling the pressure is shown in figures 2 and 3. The apparatus shown in figure 2 operates on the principle that the flask packed in ice will always bring the trapped air to the same volume. Hence the external pressure will always have to be the same at R in order to close the tungsten-mercury contact in the capillary tube.

Figure 3 shows the artificial atmosphere which was used to maintain a constant pressure on the volumetric apparatus.

The principle on which this apparatus works is as follows: Compressed air is admitted at C by means of a constant-pressure reducing valve set at a pressure of 10 lb. The magnetic valve G being open, as is the stopcock V when the air is turned on, the air passes over into the bottle B and there builds up pressure until contact is made by the mercury contact in the pressurestat shown in figure 2. This contact closes the solenoid circuit and the magnetically operated ground valve G is drawn into place and closed. V is then closed, and the two needle valves N are adjusted until the amount of air leaving the valve connected to the large bottle is slightly greater than the amount getting through G when it is closed; thus the pressure falls and the contact is broken in the pressurestat. This opens the valve G, and more air now goes through the needle valve

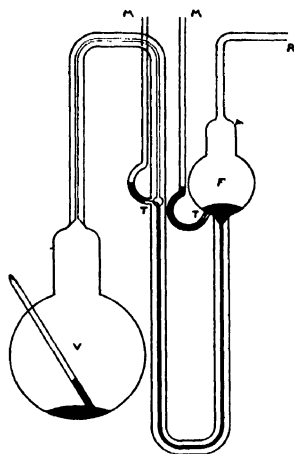


FIG. 2

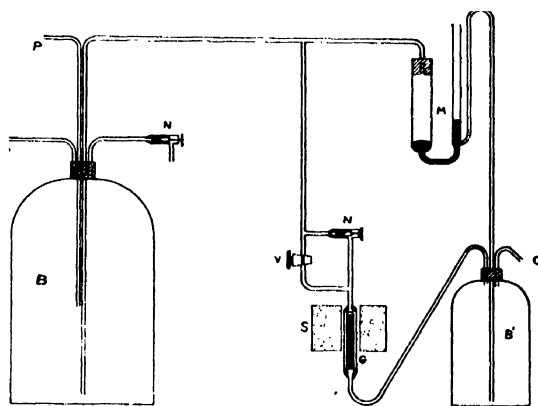


FIG. 3

FIG. 2. Apparatus used in controlling the pressure

FIG. 3. Artificial atmosphere used to maintain a constant pressure on the volumetric apparatus

above G than can escape through the other needle valve; hence the pressure builds up until contact is made in the pressurestat, again closing G. When G is closed the air escapes through the mercury bubbler M.

Since the solenoid is connected to 110 volts d.c., an amplifier and relay are used to prevent sparking of the mercury contact in the pressurestat. The relay used was one that closed on 12 milliamperes and opened cleanly on 3 milliamperes or less.

The volumetric apparatus was maintained at a constant temperature by having the volumetric flask immersed in mineral oil contained in a vessel insulated with rock wool. The heater in this bath was controlled by a mercury regulator which operated a relay connected to an amplifier.

The pressurestat was calibrated by hooking it up to the artificial atmosphere, which in turn was connected to a precision barometer. The

pressurestat was packed in ice and the difference in levels of the barometer was read with a cathetometer. It was found that, with the contact in the pressurestat making and breaking at five-second intervals, no movement of the mercury levels was visible through the cathetometer; this indicated that the apparatus was maintaining the pressure constant to 0.02 mm. The pressure maintained was 760.44 mm.

The principle involved in making a vapor density determination with the apparatus described is very simple. It merely involves getting a known volume of vapor under known conditions of temperature and pressure and then condensing this vapor into a weighing bottle and weighing it.

After the vapor has been brought to constant conditions in the volumetric apparatus the flask is cut off from the rest of the system by closing stopcocks 2 and 3. The connecting tubes are cleaned out by drawing dry air through them. The air is dried by passing it through a calcium chloride tube and then through a spiral containing a filter immersed in liquid air. The weighing bottle is immersed in liquid air, and the vapor in the volumetric flask is drawn over into the weighing bottle and frozen out by the liquid air. The weighing bottle is then weighed, and the four quantities necessary for the calculation of the vapor density are then available.

PURIFICATION OF MATERIALS

The authors were very fortunate in having very pure liquids at hand with which to work. All of the alcohols which were used in the vapor density measurements had been purified by Mr. Morgan Rarick of the Department of Chemistry, University of Kansas.

These alcohols had been purified chiefly by fractional distillation and fractional freezing. Their purity was checked by determining their physical constants and also by the use of Cady's vapor density machine, which is a sensitive device for the determination of the purity of liquids.

The deuterium oxide used was obtained from the Stuart Chemical Co., San Francisco, and was listed as 99.9+ per cent D_2O ; its density at 25°C. was 1.1079 g. per cubic centimeter.

METHOD OF CALCULATION

The calculation of molar weights from the data obtained is accomplished by a transposition of the well-known perfect gas equation:

$$M = \frac{mRT}{PV}$$

The author concludes that the results calculated from the data taken may be taken as accurate to 0.03 of a molar weight unit for the alco-

hols and 0.05 of a molar weight unit for water and deuterium oxide. These figures were obtained from a consideration of the following facts: the temperature may be taken as accurate to $0.1^{\circ}\text{C}.$, the pressure is known

TABLE 1

Molar weights of alcohols, water, and deuterium oxide

TEMPERATURE	VOLUME	MASS	MOLAR WEIGHT	TEMPERATURE	VOLUME	MASS	MOLAR WEIGHT
Data for methyl alcohol, formula weight 32.03, b.p. $64.5^{\circ}\text{C}.$				Data for <i>n</i> -butyl alcohol, formula weight 74.08, b.p. $117.7^{\circ}\text{C}.$			
$^{\circ}\text{C}.$	cc.	grams		$^{\circ}\text{C}.$	cc.	grams	
66.2	512.15	0.6214	33.76	120.1	512.43	1.2607	79.34
70.2	512.17	0.6101	33.54	122.0	512.44	1.2501	79.09
75.1	512.20	0.5986	33.38	126.1	512.46	1.2241	78.21
80.2	512.23	0.5858	33.14	131.1	512.49	1.1932	77.18
85.3	512.25	0.5737	32.92	136.0	512.52	1.1646	76.24
Data for ethyl alcohol, formula weight 46.05, b.p. $78.5^{\circ}\text{C}.$				Data for water, formula weight 18.016, b.p. $100.0^{\circ}\text{C}.$			
82.0	512.23	0.8423	47.89	101.9	512.34	0.3102	18.62
86.0	512.25	0.8308	47.77	104.0	512.35	0.3085	18.62
90.0	512.27	0.8190	47.61	108.0	512.37	0.3050	18.61
95.0	512.30	0.8051	47.44	112.0	512.39	0.3016	18.59
100.0	512.33	0.7916	47.28	117.0	512.41	0.2974	18.57
Data for <i>n</i> -propyl alcohol, formula weight 60.06, b.p. $97.8^{\circ}\text{C}.$				122.0	512.44	0.2935	18.56
100.1	512.33	1.0590	63.27	132.0	512.49	0.2849	18.47
104.0	512.35	1.0440	63.02	Data for deuterium oxide, formula weight 20.032, b.p. $101.4^{\circ}\text{C}.$			
107.9	512.37	1.0296	62.80	104.0	512.35	0.3440	20.77
113.0	512.40	1.0125	62.57	106.0	512.36	0.3415	20.72
118.0	512.42	0.9956	62.32	109.8	512.38	0.3365	20.62
Data for isopropyl alcohol, formula weight 60.06, b.p. $82.3^{\circ}\text{C}.$				115.0	512.40	0.3319	20.61
83.9	512.24	1.1037	63.09	123.4	512.45	0.3234	20.52
86.3	512.26	1.0927	62.88				
90.0	512.27	1.0777	62.67				
95.1	512.30	1.0594	62.44				
102.0	512.35	1.0364	62.23				

to 0.02 mm., the volume to 0.01 cc., and the mass to one part in two thousand in the case of the smallest amount of liquid weighed.

DATA

In all of the cases reported the mass recorded in table 1 is the average of at least three trials. The pressure was the same during all runs and

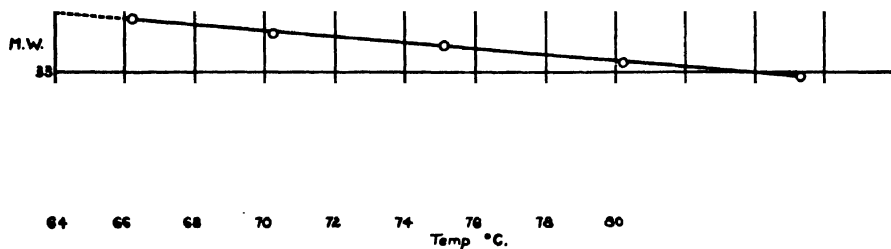


FIG. 4. Plot of data for methyl alcohol

18.0
M.W.
47.4

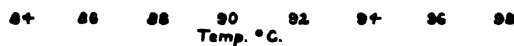
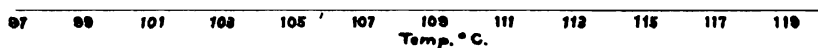


FIG. 5. Plot of data for ethyl alcohol

63.4
63.4
M.W.
62.6
62.2

FIG. 6. Plot of data for *n*-propyl alcohol

was 1.0006 atm. The volumes recorded are those calculated from the calibration volume by use of the cubical coefficient of expansion of Pyrex.

The data of table 1 are shown in a graphical manner in figures 4 to 10.

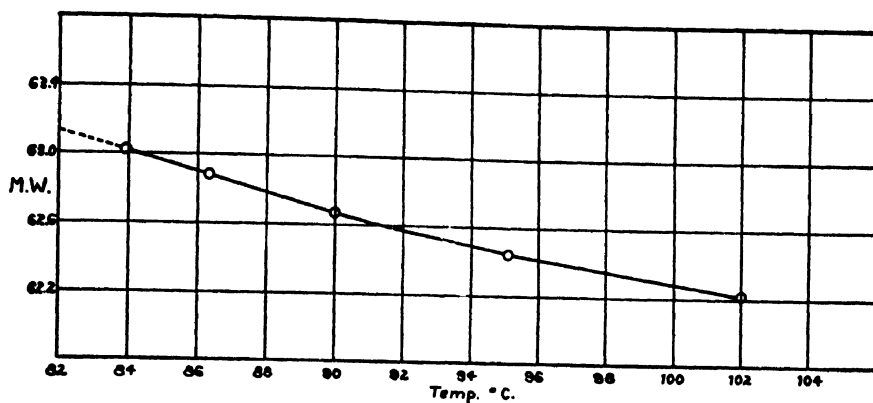


FIG. 7. Plot of data for isopropyl alcohol

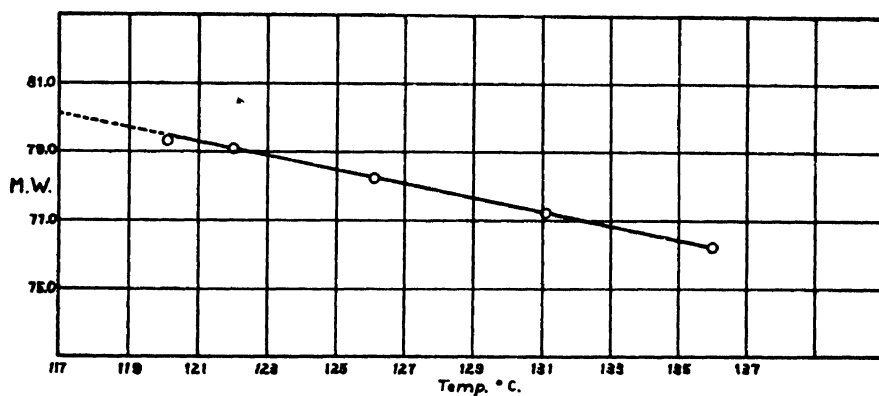


FIG. 8. Plot of data for n-butyl alcohol

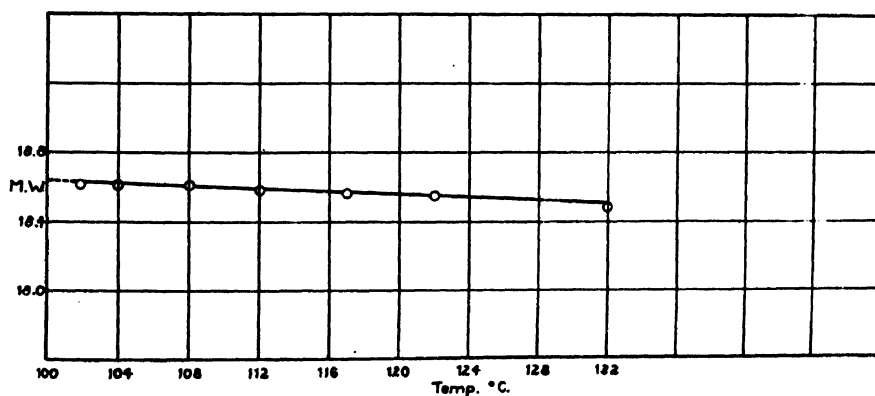


FIG. 9. Plot of data for water

In all cases the calculated molar weights are plotted as a function of temperature and are extrapolated back to the boiling point of the liquid in question. This extrapolation should be quite accurate, as Rankin (5)

showed in his work that if the molar weights close to the boiling point were corrected for adsorption on the glass, the curves continued as a straight-line function of temperature. His data also showed that adsorption had no effect on the molar weights until the vapor was down to within 2° of the boiling point, in the case of the alcohols and water.

Table 2 shows the molar weights extrapolated to the boiling points of the liquids.

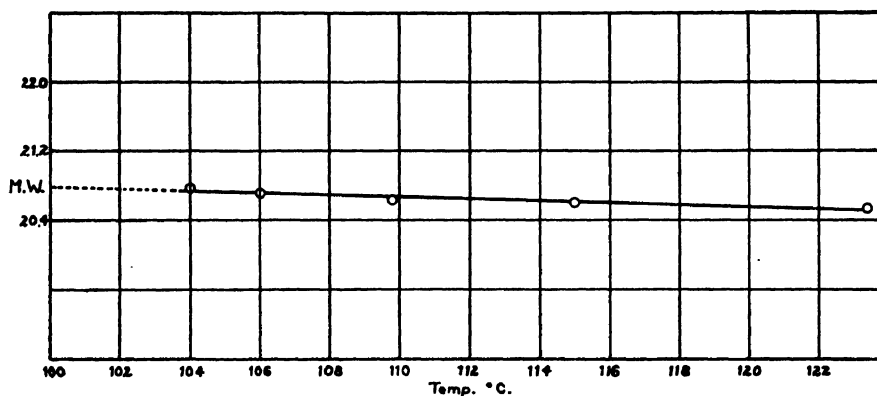


FIG. 10. Plot of data for deuterium oxide

TABLE 2

Molar weights extrapolated to the boiling points of the liquids

SUBSTANCE	FORMULA WEIGHT	EXTRAPO- LATED MOLAR WEIGHT	DIFFERENCE	BOILING POINT °C.
Methyl alcohol.....	32.03	33.82	1.79	64.5
Ethyl alcohol.....	46.05	48.07	2.02	78.3
<i>n</i> -Propyl alcohol.....	60.06	63.34	3.28	97.8
Isopropyl alcohol.....	60.06	63.12	3.06	82.3
<i>n</i> -Butyl alcohol.....	74.08	79.95	5.87	117.7
Water.....	18.02	18.64	0.62	100.0
Deuterium oxide.....	20.03	20.78	0.75	101.4

DISCUSSION

A consideration of the data and curves indicates that when the molar weights of extremely pure liquids are plotted against temperature, the values of molar weights seem to fall in an almost linear manner with increasing temperature.

It should be remembered that the temperature ranges studied were only about 30° at the most. It is evident that the relationship between molar weight and temperature must change from this straight-line function as the temperature is increased more and more. The rate of change

of molar weight with temperature must decrease until a temperature is reached at which the molar weight becomes equal to the formula weight.

A survey of the data presented shows clearly that the molar weights of the liquids at their boiling points are invariably higher than the formula weights of the liquids. It should be remembered that these molar weights were calculated using the perfect gas equation, and hence they would be expected to differ from the formula weights.

Two explanations of these differences are possible. Either the vapors are "associated," i.e., have double or triple molecules present, or else the individual molecules have stronger forces acting between them than predicted by the gas laws. Both of the above assumptions will give an apparent explanation of the experimental results, because it may be assumed that an increase in temperature would increase the degree of dissociation of the polymolecules and hence give smaller apparent molar weights with increasing temperature. On the other hand, it might be assumed that an increase in temperature increases the kinetic energy of the individual molecules and hence increases the distance between them, this leading to smaller apparent molar weights as the temperature increases.

Bose (1) has made calculations concerning the association of water vapor under its own vapor pressure. At a temperature of 100.0°C. he calculated a degree of dissociation equal to 0.911, assuming that the water vapor was a mixture of single and double molecules. Using the same equation used by Bose the writer obtained a degree of dissociation of double molecules of water at the boiling point and under a pressure of 1.0006 atm. equal to 0.933. A similar calculation made for deuterium oxide yields a value of 0.928. From this result it might be assumed that the attractive forces are slightly greater between the deuterium oxide molecules than between those of water.

It is interesting to note that van der Waals equation

$$(p + a/v^2) (v - b) = RT$$

does not correctly express the P-V relationships of water vapor at its boiling point under a pressure of 1.0006 atm. The constants a and b are evidently much too small for these conditions.

New constants have been calculated for the equation, using our vapor density data. The authors found that the value of a obtained was about five times as large as that given in the Landolt-Börnstein Tables, while the value of b was about twice as large as the value ordinarily used.

It has been previously mentioned that values of molar weights at the boiling point would be useful in calculating heats of vaporization.

The Clapeyron equation shown below is not easy to integrate, because V

and v are functions of pressure and temperature while l is a function of temperature also.

$$\frac{dP}{dT} = \frac{(l \times M.W.)}{T(V - v)}$$

The above equation is usually integrated after making several simplifying assumptions, such as setting v equal to zero as v is very small compared to V , and taking V as equal to RT/P . The latter assumption is perfectly correct if the molar volume is defined as RT/P , which is precisely what is done in calculating the molar weights at the boiling point, i.e., the molar weight is defined as the weight of the substance that occupies a volume RT/P cubic centimeters. After making these assumptions the

TABLE 3
Latent heats of vaporization per gram

SUBSTANCE	l (CALCULATED)	l (FROM INTERNATIONAL CRITICAL TABLES)
	<i>cal. per gram</i>	<i>cal. per gram</i>
Methyl alcohol.....	270.3	262.8
Ethyl alcohol.....	207.2	204
<i>n</i> -Propyl alcohol.....	164.5	162.5
Isopropyl alcohol.....	156.1	159
<i>n</i> -Butyl alcohol.....	139.5	141
Water.....	530.1	539.55 •

equation may be integrated if it is assumed that l is independent of temperature, and takes the following form

$$\ln P = -(l \times M.W.)/RT + \text{constant}$$

This equation omits the molar volume of the liquid at the boiling point and hence is not an exact equation.

Rankin (5) has shown that it is possible to integrate the Clapeyron equation without omitting the molar volume of the liquid, and that the equation obtained is too complex and awkward to be used for the calculation of heats of vaporization.

Going back to the differential form of the equation it may be seen that the desired calculations cannot be made from values of P and T alone, but that there must also be a knowledge of dP/dT . The method of obtaining dP/dT values by plotting P against T and determining the slope by means of a tangentimeter has been suggested by Latshaw (2), but it has been found very difficult to get accurate values by this method. It has been found that more accurate values may be obtained by the use of an analytical method.

Rankin (5) has shown that the equation

$$\frac{dP}{dT} = \frac{LP}{RT^2}$$

obtained from the Clapeyron equation by neglecting the molar volume of the liquid is valid for this type of work, since L may be established from vapor pressure data.

It is not necessary actually to calculate dP/dT because it may be shown that the true molar heat of vaporization, L' , is related to the arbitrary constant, L , by the equation,

$$L' \equiv \frac{L(V - v)}{V}$$

In using this equation it should be remembered that the molar volume of the vapor at the boiling point has been previously defined as RT/P cubic centimeters. L , as shown above, may be determined from vapor pressure data, and v may usually be found in orthobaric density tables.

In order to obtain l , L' must be divided by the molar weight of the substance at its boiling point, as found experimentally.

Table 3 contains the latent heats of vaporization per gram as calculated by the method shown above. The values given in the International Critical Tables are also given for comparison.

An inspection of table 3 shows that the values of l calculated as described above agree fairly well with those given in the International Critical Tables. With the exception of the value of l calculated for water the authors feel that the values reported here are more accurate than any previously reported. The relatively low value of l calculated for water is indeed puzzling, and the authors have no explanation to offer.

SUMMARY

1. The Dumas method of determining molar weights from vapor density measurements has been improved upon so that molar weights may be determined at the boiling point.

2. The molar weights of water, deuterium oxide, and several aliphatic alcohols have been determined at their boiling points.

3. The heats of vaporization of the above substances have been determined by use of the molar weights at the boiling points and of vapor pressure data.

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MOBILITY STUDIES WITH COLLOIDAL SILICIC ACID¹

FRED HAZEL²

Department of Chemistry, University of Wisconsin, Madison, Wisconsin

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The mutual reactions of colloids attending the mixing of systems of opposite sign have been investigated by electrokinetic methods (1, 2, 3, 7). Of these, the method employing the ultramicroscope offers a distinct advantage, since mobilities of mixed systems can be observed throughout the concentration range including the flocculation zone. Accordingly, it is possible to study the mutual coagulation process as well as the mutual effects produced by varying concentrations of components in stable mixtures. In the latter case information can be obtained relating to the change in stability of the components and, in a restricted sense, to changes in the state of the particles, e.g., whether the components are completely independent, or combined (owing to capillary-active properties), or partially combined and partially free (7).

Weiser and Chapman (9) are of the opinion that the mutual coagulation process may be determined by a number of factors: namely, electrical neutralization, mutual adsorption of the particles, interaction between stabilizing ions, and the presence of excess electrolyte in the sols. These same factors probably influence the state of the particles in stable mixed systems. On the other hand, exponents of a chemical mechanism explain mutual coagulation as a result of a reaction between the stabilizing electrolytes. Thus Thomas and Johnson (8) found for the undialyzed system ferric oxide-silicic acid that coagulation was at an optimum where the concentrations of sodium hydroxide and hydrochloric acid were equivalent.

Hazel and McQueen (3) investigated the electrophoretic behavior of mixtures obtained from a number of oppositely charged sols and, although no silicic acid sols were employed, they were led to a mechanism for mutual coagulation that supported Weiser's conclusions. Furthermore, it was observed in the coagulation zones and in the stable regions on either side that the particles of the mixed systems possessed a single mean velocity

¹ This research was supported by a Grant-in-Aid from the Graduate School of the University of Wisconsin.

² Present address: Harrison Laboratory, University of Pennsylvania, Philadelphia, Pennsylvania.

value, indicating that the oppositely charged components had completely combined with each other.

The present study is concerned with the electrophoretic properties of silica sols and of mixtures of silica sols with colloidal ferric oxide and aluminum oxide. These systems, in various states, comprise the major part of the inorganic fraction of soil colloids.

PREPARATION OF SOLS

The silica sol used in the present investigation was prepared by Graham's method. The aluminum oxide sol was made by small additions of *N*/20 hydrochloric acid to the precipitated oxide with alternate boiling. The iron oxide sol was prepared by hydrolysis of ferric chloride in boiling water. All of the sols were dialyzed for one week in collodion sacs. Data on the sols are given in table 1.

TABLE 1
Data on the sols

SOL	TEMPERATURE OF DIALYSIS	pH OF DIALYSATE	CHLORIDE TEST	CONCENTRATION (STOCK)
	°C.			grams per liter
Silica	22-25	4.75	Trace	10.0
Aluminum oxide.....	22-25	6.5	Trace	2.3
Ferric oxide.....	70-90	5.5	Trace	1.9

EXPERIMENTAL

Electrophoretic measurements were carried out by an ultramicroscopic method previously described (5). A velocity-depth curve was constructed, and the value for the true mobility obtained from the area under the curve was found to agree with that observed at the calibrated 0.147 level. In ascertaining the mean velocity values, ten readings were taken in alternate directions of the time required for a particle to traverse 200 μ under a potential gradient of 8.0 volts per centimeter. The distance between the electrodes was 11.75 cm.

Hydrogen-ion activities were determined with a glass electrode.

The "visibility" of the particles varied considerably with the three colloids. Thus the particles of the silica sol were poorly resolvable, while those of the aluminum oxide sol appeared very distinct.

RESULTS

The effect of hydrogen-ion activity on the mobilities of colloidal silica and of aluminum oxide are shown in figure 1. Adjustments of pH were made with hydrochloric acid or with sodium hydroxide. The concentra-

tion of silica in this experiment was 1.00 g. per liter, and that of aluminum oxide was 0.23 g. per liter. Data for a purified, naturally occurring, hydrogen-saturated aluminum bentonite are also included for comparison. These are shown as black dots in figure 1. The bentonite had a silica-alumina ratio of about four to one, and its concentration was 0.024 g. per liter. The silica and bentonite curves are characterized by the fact that neither is recharged at the higher acidities, resembling arsenic trisulfide in this respect (3).

The aluminum oxide curve is similar in form to that obtained with iron oxide (5) under like conditions.

In table 2 are shown mobility data for colloidal silica with electrolytes. The potential of the particles is decreased markedly by small additions of electrolytes, and the valency effect conforms to that usually found for negative colloids. It is noteworthy, however, that the negative character

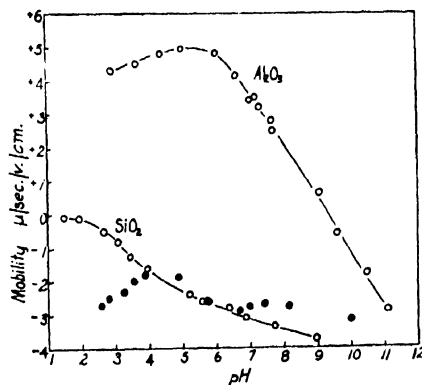


FIG. 1. The effect of hydrogen-ion activity on the mobilities of colloidal silica and aluminum oxide

of the sol seems to be permanent, as is evidenced in the behavior with aluminum chloride.

The effect of electrolytes of different valence types on the mobilities of the aluminum oxide and ferric oxide sols that were used in later experiments with mixed systems was found to be quite normal and is not reported here.

Data are given in table 3 for systems obtained by mixing colloidal silica and alumina in the proportions indicated. Table 4 gives similar data for colloidal silica-ferric oxide mixtures.

The mobilities in tables 3 and 4 are plotted in figure 2.

The sols employed in these experiments, when diluted to the concentrations used in preparing the mixtures, all had a pH of close to 5.1. They were well dialyzed, which cut down the presence of free electrolytes to a minimum.

It is to be noted, from figure 2, that aluminum oxide is much more effective in discharging silica than is ferric oxide. Thus when alumina, which

TABLE 2
Mobility data for colloidal silica with electrolytes

ELECTROLYTE CONCENTRATION IN MILLIMOLES PER LITER	MOBILITY IN μ PER SECOND PER VOLT PER CENTIMETER	
	NaCl	KCl
0	-2.3	-2.3
2	1.6	1.4
4	1.0	0.9
8	0.7	0.7
16	0.5	0.4
	CaCl ₂	BaCl ₂
0	-2.3	-2.3
0.16	1.2	1.1
0.4	1.0	0.8
1.4	0.8	0.7
5.0	0.5	0.4
	AlCl ₃	
0	-2.3	
0.02	2.1	
0.04	1.5	
0.1	0.7	
0.3	ca. 0.1 (coagulated)	
0.6	0.0 (coagulated)	

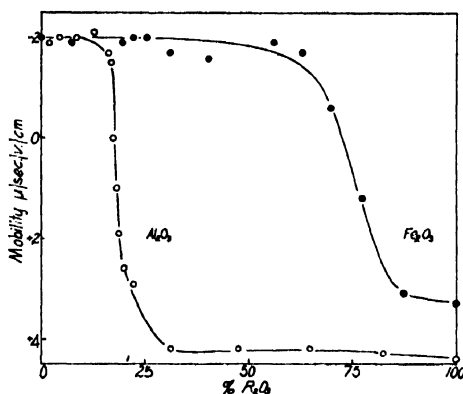


FIG. 2. Mobilities for systems obtained (a) by mixing colloidal silica and alumina and (b) by mixing colloidal silica and ferric oxide.

had the higher electrokinetic potential, is present to the extent of 17 per cent the mixture is isoelectric, whereas more than 70 per cent of ferric oxide is required to produce the same result. It is not probable that this

wide difference in effectiveness can be accounted for on the basis of a chemical mechanism of reaction between stabilizing ions, because this

TABLE 3

Data for systems obtained by mixing colloidal silica and alumina

PER CENT OF Al_2O_3	MOLECULAR RATIO OF SiO_2 TO Al_2O_3	MOBILITY IN μ PER SECOND PER VOLT PER CENTIMETER		
0		-2.0		Few particles "visible"
1.9	88.7	1.9		Number of "visible" particles
4.5	35.5	2.0		increasing
8.7	17.7	2.0		Number of "visi-
12.6	11.8	2.1		ble" particles
16.1	8.9	1.7		decreasing
16.8	8.5	1.5		Coagulation
17.4	8.1	± 0.0		Coagulation
18.1	7.7	+1.0		Coagulation
18.7	7.4	+1.9	+4.3*	Coagulation
20.0	6.8	+2.6	+4.5*	"Visible" parti- cles increasing in number
22.3	5.9	+2.9	+4.5*	
31.0	3.8	+4.2	+1.8*	
47.4	1.9	+4.2	+2.0*	
64.3	0.94	+4.2	+2.8*	Coagulation
81.8	0.38	+4.3		
100		+4.4		

* Two sets of velocity values.

TABLE 4

Data for systems obtained by mixing colloidal silica and ferric oxide

PER CENT OF Fe_2O_3	MOLECULAR RATIO OF SiO_2 TO Fe_2O_3	MOBILITY IN μ PER SECO PER VOLT PER CENTIMET		
0		-2.0		
7.5	33.1	1.9		
19.5	11.0	1.9		
22.0	9.5	2.0		Coagulation
25.3	7.9	2.0		Coagulation
31.1	5.9	1.7		Coagulation
40.4	4.0	1.6		Coagulation
57.5	2.0	1.9		Coagulation
62.9	1.6	1.7		Coagulation
69.3	1.2	0.6		Coagulation
77.2	0.8	+1.2		Coagulation
87.1	0.4	+3.1	+1.4*	
100		+3.3		

* Two sets of velocity values.

would necessitate postulating a marked difference in solubility of the silicates.

DISCUSSION

It was observed in the present study that the particles of colloidal silicic acid were poorly "visible" in the ultramicroscope. This was to be expected from the well-known fact that silica sols are heavily hydrated. As in the case with gelatin (6) the "visibility" of the particles was enhanced by addition of a hydrophobic colloid up to a certain limit and, similarly, small additions of oppositely charged hydrophobic colloids were without effect on the mobility of the silica particles. This behavior is in marked contrast to that obtained when two oppositely charged hydrophobic colloids are mixed (3).

An inspection of the data in table 3 shows that coagulation began before the particles in the mixed system had experienced any apparent diminution in mobility. These data cannot be used, however, either against or to support the idea of a critical potential. Addition of aluminum oxide up to a silica-alumina ratio of 11.8 did not reduce the mobility of the stable colloid particles, but it did reduce the number of these stable particles. The mobility of the large flocs could not be obtained with accuracy.

The state of the system was definitely heterogeneous throughout the concentration ranges where coagulation took place (except possibly at zero mobility) and where two mean sets of mobilities were observed. The experimental evidence further suggests that the components were present as (1) adsorption complexes and, depending upon which was in excess, as (2) free alumina or free silica. The results with the colloidal silica-iron oxide mixture were analogous to those obtained with silica-aluminum oxide mixtures.

SUMMARY

1. An electrokinetic study of colloidal silicic acid has been made with the aid of an ultramicroscope.
2. The effect of electrolytes, pH, and of colloids of opposite sign on the mobility has been investigated.

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ON THE KINETICS OF TYROSINE DESTRUCTION AND DOPA FORMATION BY ULTRA-VIOLET RAYS

L. EARLE ARNOW

*Laboratory of Physiological Chemistry, University of Minnesota,
Minneapolis, Minnesota*

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One of the products produced when *l*-tyrosine is destroyed by ultra-violet radiant energy is dopa (3,4-dihydroxyphenylalanine) (2). In the experiments described in this paper, tyrosine and dopa have been determined by methods previously reported by the author (1). The only significant modification in the analytical procedure consisted in the use of a compensation cup¹ in the dopa determinations. This was necessary because the irradiated solutions developed a brown color. This color was precipitated by the reagents used in determining tyrosine, and did not interfere with the determination of this compound.

A Victor therapy quartz-mercury arc (air-cooled)² was used as a source of ultra-violet radiant energy. This instrument, as used, operated with a voltage drop of 65 to 70 volts across the quartz-mercury tube. All solutions were irradiated at a distance of 30 cm. from the light source. In a preliminary experiment 20 cc. of tyrosine solution, containing 22.1 micromoles of tyrosine, was placed in a test tube. The tube was loosely stoppered and immersed in a boiling water bath for 6 hours. Since no dopa was formed by this procedure, the solutions exposed to the lamp were not cooled. In general, the temperature of the solutions undergoing irradiation quickly rose to about 48–50°C. and remained practically unchanged until the lamp was turned off.

The kinetics of the reactions were investigated by placing 20-cc. portions (containing 22.1 micromoles of tyrosine in distilled water) of tyrosine solution in well-corked clear quartz test tubes (25-cc. capacity) and exposing these solutions to the radiant energy for varying lengths of time.

KINETICS OF TYROSINE DESTRUCTION

The results of tyrosine analyses are given in table 1. *T* represents micromoles of tyrosine present in the 20 cc. of solution, *t* represents time, and

¹ For a description of the use of the compensation cup see J. F. McClendon (A Manual of Biochemistry, p. 305. John Wiley and Sons, New York (1934)).

² This lamp was made available to the author through the courtesy of Dr. W. K. Stenström and the University of Minnesota Hospitals.

D represents micromoles of dopa present in 20 cc. of solution. If $\log T$ is plotted graphically as a function of t , a straight line results. The differential equation relating T and t is thus

$$-\frac{dT}{dt} = k_1 T,$$

in which k_1 is the velocity constant of the reaction (t is measured in hours). The integrated form of this expression is

$$T = T_0 e^{-k_1 t}$$

where T_0 refers to the amount of tyrosine initially present in 20 cc. of solution. The value of k_1 , calculated from the data, is 0.071. Calculated values of tyrosine are given in table 1.

TABLE 1

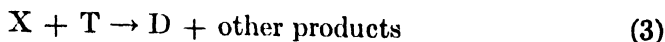
Destruction of tyrosine and formation of dopa by ultra-violet rays

t	T (ANALYTICAL)	T (CALCULATED)	D (ANALYTICAL)	D (CALCULATED)
hours	micromoles in 20 cc.	micromoles in 20 cc.	micromoles in 20 cc.	micromoles in 20 cc.
0	22.1			
1	20.1	20.1	0.4	0.5
2	19.4	19.2	0.7	0.7
3	18.1	17.9	1.2	1.2
4	16.4	16.6	1.9	1.6
6	14.4	14.5	2.2	2.1
12	8.8	9.4	2.6	2.5
15.8	7.2	7.2	2.8	2.8

The above equations indicate that the destruction of tyrosine in these experiments occurred as a first-order reaction. Verification of this conclusion was obtained by irradiating tyrosine solutions of different initial concentrations for 4 hours. The results are given in table 2. These data indicate that the fraction of tyrosine still present in a given time interval was independent of the initial concentration, a necessary condition of first-order reactions.

The absorption spectrum of tyrosine in aqueous solution is given in the International Critical Tables (3). The molecular extinction coefficients of tyrosine vary from about 5900 at 2800 A. U. to about 1000 at 2460 A. U. McAlister's (4) data indicate that there are four strong mercury emission bands in this region: at 2804, 2652, 2536, and 2483 A. U., respectively. The emission bands at 2967 A. U. and 3022 A. U. are relatively of much less importance, because the molecular extinction coefficients of tyrosine at these wave lengths are relatively low. Calculations using these figures show that practically all the radiant energy between 2460 A. U. and 2800 A. U. is absorbed by the tyrosine solutions undergoing irradiation. This

fact suggests that the mechanism of tyrosine destruction may be of the type indicated by the following equations, in which X represents an active intermediate:



If reaction 2 is rapid as compared with reaction 3, this series of reactions would result in a first-order destruction of tyrosine. In the above argument it is tacitly assumed that an unlimited supply of oxygen is available, a condition which is met by the experimental procedure, since a large excess of oxygen is always present. No tyrosine is destroyed in a 4-hour period when tyrosine solutions are irradiated *in vacuo*.

TABLE 2
Destruction of tyrosine in a 4-hour period

T_0	T	$\frac{T}{T_0}$
<i>micromoles in 20 cc.</i>	<i>micromoles in 20 cc.</i>	
5.5	4.1	0.75
11.1	8.3	0.75
22.1	16.4	0.74

KINETICS OF DOPA FORMATION

The rate of dopa formation should be given by the equation

$$\frac{dD}{dt} = a \frac{dT}{dt}$$

where D refers to the micromoles of dopa formed in the irradiated solution, and where a is a constant. If a is 1, each molecule of tyrosine which is destroyed results in the formation of a molecule of dopa; if a is less than 1, it represents the fraction of destroyed tyrosine molecules which form dopa.

One isolated experiment which illustrates that dopa is destroyed by the radiant energy was performed. Twenty cubic centimeters of dopa solution (containing 5.07 micromoles of dopa) was exposed to the lamp for 4.5 hours. Analysis showed that 29 per cent of the dopa had been destroyed. No tyrosine had been formed. If it is assumed that the destruction of dopa is a first-order reaction,

$$-\frac{dD}{dt} = k_2 D$$

where D represents micromoles of dopa present at time t , and k_2 is the velocity constant.

If the above assumptions are made, the rate of change of dopa in irradiated tyrosine solutions is given by the expression,

$$\frac{dD}{dt} = ak_1T - k_2D$$

Integrating this expression,

$$D = \frac{k_1}{k_2 - k_1} aT_0[e^{-k_1t} - e^{-k_2t}]$$

The only unknowns in this equation are a and k_2 . If data are taken from several points on the dopa-time curve, and the resulting equations are solved for a and k_2 , the following expression results:

$$D = \frac{0.071}{0.074 - 0.071} \frac{T_0}{3} [e^{-0.071t} - e^{-0.074t}]$$

This equation appears to approximate the experimental data fairly well. Calculated and analytical values for dopa are compared in table 1. This equation can be interpreted to indicate that one-third of the tyrosine molecules which are destroyed are converted to dopa; and that the destruction of dopa is of the first order, the velocity constant having a value of 0.074.

The author wishes to thank Dr. Robert S. Livingston for his kindness in assisting the author in the interpretation of the data presented in this paper.

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METALLIC COUPLES. II

CONCERNING THE PREPARATION OF ALUMINA HYDROSOLS^{1,2}

MIKE A. MILLER

*Aluminum Research Laboratories, Aluminum Company of America,
New Kensington, Pennsylvania*

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INTRODUCTION

The author has recently pointed out (35) that practically pure alcoholic alumina jellies can be prepared by a modification of the Kutzelnigg-Wagner reaction (32). Kutzelnigg and Wagner allowed a 2 per cent copper chloride solution in 95 per cent ethyl alcohol to act on metallic aluminum in order to produce an alcoholic alumina gel. Analysis showed the final transparent product to be free from copper ion but to contain a high percentage of chloride ion. The modified method, described by the present author (35), produced gels apparently free from both of these ions. Further studies have indicated that an extension of the modified method can be used to prepare reasonably pure colloidal alumina.

The purpose of the present note is to describe a simple method of preparing large quantities of apparently unprotected, but remarkably stable, alumina hydrosols. Preliminary work on other than the aluminum-copper couple is described, and a mechanism for the reaction is proposed. Data for rate of settling of alumina hydrosols are given.

ALCOHOL-ACTIVATED ALUMINUM-COPPER COUPLE

The Kutzelnigg-Wagner reaction (32) was allowed to proceed for several days. The copper-coated aluminum sheet was then removed, washed thoroughly in alcohol, and placed in distilled water. After several days an alumina hydrosol-producing couple was obtained. The first portion of the hydrosol was discarded, as it contained some copper, and fresh water was added. As the hydrosol concentration became of sufficient strength for whatever purpose it was intended, it was filtered through fine-pored filter paper into a steamed flask or stock bottle.³ More distilled

¹ Metallic Couples. I. Über kolloides Kupfer und alkoholisches Aluminiumoxyd Gel. Kolloid-Z. [3] 77, 310-12 (1937).

² The experimental work described in this paper was carried out in the Chemical Laboratories of the University of Michigan, Ann Arbor, Michigan, 1932-36.

³ Since the hydrosol appears to be very sensitive to traces of electrolytes, care should be taken to steam all containers, if flocculation is to be avoided.

water was added to the couple each time. In this manner, with occasional stirring, such couples continued to produce the hydrosol until virtually all of the metallic aluminum was used up. The resulting hydrosols were neutral to litmus. Hydrosols containing up to 1 g. of Al_2O_3 per liter have been prepared.

REACTIONS OF OTHER METALLIC COUPLES

Table 1 summarizes data relative to the physical character of the alumina produced by several metallic couples in various media. The couples were made as follows: Sheets of 99.5 aluminum (ca. 2 in. x 1 in.)

TABLE 1

Physical character of alumina from several metallic couples

METALLIC COUPLE	METHOD OF PREPARING COUPLE: ALUMINUM SHEET IN	FORM OF PRODUCT IN GIVEN MEDIA		
		Distilled H_2O	0.02 N AlCl_3	95 per cent ethyl alcohol
Al-Hg	Aqueous HgCl_2	Fibrous	Hydrosol	Flocculent
Al-Cd I	Aqueous acidic CdCl_2		Flocculent	
Al-Cd II	Alcoholic CdCl_2	Trace of hydrosol	Trace of hydrosol	
Al-Cu I	Aqueous CuCl_2	Fine, flocculent	Hydrosol	Gel
Al-Cu II	Alcoholic CuCl_2	Hydrosol	Hydrosol	Gel
Al-Cu III	CuAl_2 intermetallic compound	Gelatinous	Flocculent	Trace of gel; coarse black precipitate
Al-Fe I	Aqueous acidic FeCl_3	Coarse, flocculent	Fibrous	Gel
Al-Fe II	Alcoholic FeCl_3	Trace of hydrosol	Hydrosol	Gel
Al-Ni I	Aqueous ammoniacal NiCl_2	Hydrosol formed slowly	Hydrosol formed slowly	Trace of gel
Al-Ni II	Alcoholic NiCl_2	Hydrosol	Hydrosol	Gel

were cleaned in 5 per cent caustic, thoroughly rinsed with distilled water, and air-dried. Into each of the designated salt solutions (ca. 2 per cent) a sheet of this aluminum was then immersed for approximately one minute. After washing and air-drying, they were placed in about 50 cc. of the reaction medium and left undisturbed until the character of the product was apparent. In general, this period did not exceed two weeks.

Besides the couples listed in table 1, a preliminary investigation was made on couples of aluminum with tin, zinc, cobalt, lead, and silver. Of these only the aluminum-cobalt couple appeared to produce hydrosols in pure water.

From table 1 it is apparent that the manner of preparing the couple is

of more than minor importance. The particle size of the deposited metal, the porosity of the coating, and the activity of the deposited metal are evidently functions of the deposition medium. Factors such as the concentration of the depositing solutions and the effect of the temperature of deposition and of reaction, of the pH of the depositing solutions, of the thickness of the metallic coating, and of colloids were not investigated. In the opinion of the author, these factors have an important bearing on the decomposition of water by metallic couples.

We note that in contrast to the well-known aluminum-mercury couple (6, 49), which ordinarily produces with water a flocculent, fibrous alumina (39, 50), and evidently produces true sols (41) only in the presence of stabilizing ions, the alcohol-activated aluminum-copper couple generates a remarkably stable, apparently unprotected hydrosol. Experiments performed with an aluminum-copper couple which had been generated in an aqueous cupric chloride solution invariably resulted in the formation of flocculent alumina, incapable of more than transitory suspension in the absence of stabilizing ions. Mabb (33) has recently discussed certain reactions of the aluminum-copper couple.

The results of the interaction of various metals, including aluminum and copper, with anhydrous ethyl alcohol, gasoline, and mixtures of these two liquids, have recently been reported by Zdlarsky (51). This investigator states that ethyl alcohol which contains moisture will give a soft jelly with aluminum. The author has been unable to produce either hydrosols or gels by the action of either water or alcohol on aluminum alone. Apparently a coupled reaction is necessary (35). On the other hand, Bouchet (2) states that he has produced blue sols by allowing natural waters to react on pure zinc. It is possible that certain ions in the waters stabilized the corrosion product produced by the salts present in the waters.

SETTLING EXPERIMENTS WITH ALUMINA HYDROSOL

An attempt was made to determine the rate of settling, if any, of the hydrosol particles resulting from the interaction of the alcohol-activated aluminum-copper couple. The hydrosol used in these experiments contained 0.22 g. of Al_2O_3 per liter.⁴ Tubes of various diameters, ranging from 0.5 to 2.0 cm., were used. Evidently tube length is of more importance than tube diameter.

Some gradient settling took place and was noticeable after several weeks. No visible boundaries resulted, however, until after about three months, though a trace of sediment was apparent at the bottom of the settling tubes before this time. At the end of about six months sharp boundary effects became visible. By the proper adjustment of a light

⁴ Value obtained from calcining residue from given sol volume.

source, these boundaries could be read to within 2 mm. Representative results are recorded in table 2.

It will be seen that at first a few fairly sharp boundaries appear, that after about a thousand hours more the number has increased, and that as equilibrium is approached, several of the boundaries tend to disappear. It would be interesting to carry out similar experiments in tubes of the same diameter but of various lengths, in analogy to The Svedberg's experiments with the centrifuge.

The figures do not readily lend themselves to quantitative calculations of particle size, since no attempt was made to measure the concentration of alumina in each of the zones. Visual observation indicated that there were more particles of an intermediate size than either very small particles or very large particles. In short, the distribution was what might be expected.

Pavlov (42) has recently discussed the mechanism of coagulation. The Smoluchowski theory (43) of liquid envelopes and mutual attractions and repulsions has been further developed. It is difficult to apply the theory of velocity of coagulation to a distribution type of normal settling. One would have to assume a slow but continuous coagulation of hydrosol particles, and hence the absence of an apparent equilibrium stratification, such as was actually obtained.

DISCUSSION OF RESULTS

From a consideration of the action of water on an active metallic couple we would infer that a distribution of particle sizes would be expected. We may tentatively consider the hydrosol particles to result from the action of one or both of two series of processes. Firstly, electrochemical reaction may produce aluminum ions, which migrate into the solution before forming aluminum oxide molecules. These oxide molecules then agglomerate sufficiently to produce a range of colloidal-sized particles in agreement with experiment. The second mechanism would also begin as an electrochemical reaction, with the production of films of oxide, impermeable to aluminum ions; these films would then disrupt, under the influence of growth and pressure of generated hydrogen gas, to produce a gradation of colloidal sizes in harmony with the actual figures.

The latter mechanism seems more in keeping with experiments on aluminum-mercury couples, where the formation of films is obvious, as well as with the fact that particle sizes range from the colloidal to the macroscopic. On the other hand, the first mechanism would more adequately account for the stability of the sols, since ionic aluminum is known to peptize the fibrous alumina ordinarily produced by aluminum-mercury couples (38, 41). It is possible that alcohol-activated aluminum-copper couples produce hydrosols in pure water because of stabilization by an ethylate.

It remains to consider the individual couples. Table 3 lists the normal electrode (single) potentials and the relative hydrogen overvoltages of some of the metals investigated. The E.M.F. of a metal indicates its replacement or deposition ability; any metal will tend to replace any metal below it in the E.M.F. series. Likewise, the total E.M.F. of a cell is equal to the difference between the single electrode potentials of the electrodes. For example, the aluminum-copper couple will have an E.M.F. of 1.63 volts; the aluminum-nickel couple will have an E.M.F. of 1.06 volts.

The hydrogen overvoltages are a function of the position in the periodic arrangement of the elements, dependent upon the group. Oliverio and Belfiori (40), after investigating the decomposition of water by metals and metallic couples, conclude that this decomposition depends more on the

TABLE 3

Single potentials and relative hydrogen overvoltages of several metals

METAL	NORMAL ELECTRODE POTENTIALS	METAL	RELATIVE HYDROGEN OVERVOLT- AGES
	<i>volts</i>		<i>volts</i>
Al.....	+1.28	Zn.....	0.72
Zn.....	0.76	Hg.....	0.70
Fe.....	0.44	Cd.....	0.66
Cd.....	0.40	Al.....	0.50
Co.....	0.29	Sn.....	0.45
Ni.....	0.22	Pb.....	0.42
Sn.....	0.14	Cu.....	0.34
Pb.....	0.12	Ag.....	0.30
H.....	0.00	Fe.....	0.27
Cu.....	-0.35	Co.....	0.26
Hg.....	-0.80	Ni.....	0.24
Ag.....	-0.80		

overvoltage of the more noble metal of the couple with respect to hydrogen than on the position in the E.M.F. series. They found, for instance, that from the metals which follow zinc in the E.M.F. series only couples containing iron decompose water. These workers also investigated the effect of temperature on the decomposition of water by zinc-nickel couples, the decomposition increasing with rise in temperature.

Superficial considerations make it at once apparent that the heredity of the created couple, particularly the interagent of its formation, and the environment of the acting couple, especially the nature of the medium in which it generates the product, have also a major responsibility in determining the physical, and often the chemical, properties of the product.

This conclusion is sensibly identical with that previously advanced by the author in connection with studies on the physical character of iodine

and insoluble iodides precipitated in various media (34, 36, 37). It is notable that somewhat similar summarizations have been made as follows: (a) concerning the genesis of somatoidal aluminum oxide (25, 26, 27), basic aluminum sulfate (8, 9, 10), calcium carbonate (21, 22, 23, 24), iodides (30), and electrolytic deposits and corrosion products (28, 29) by Kohlschütter and his students; (b) regarding "memory"⁵ (12, 14, 15, 18), interaction (11, 13, 17, 19, 20, 31), and sorption (7, 16) by solid substances, especially active oxides by Hüttig and his coworkers; (c) respecting crystal polymorphism (1, 3, 4, 5) by Buerger; and (d) pertaining to spatially influenced origin and growth of various substances (44, 45, 46, 47, 48) by Urazovskii and fellow workers.

We are once more forced to the conclusion that the vectorial properties attending a given substance, by virtue of the mode of its formation, are largely responsible for the subsequent characterizations which that substance displays during the course of its chemical history. A detailed discussion of the importance of vectorialism as related to the physical and chemical character of a product and to the growth of crystals in general will be discussed in a different connection.

SUMMARY

A simple method of preparing large quantities of alumina hydrosols, apparently in the absence of stabilizing ions, has been described. It has been shown that alcohol-activated aluminum-copper couples produce sols which settle to an apparent equilibrium stratification after a period of about 5000 hours.

Preliminary experiments on other than the aluminum-copper couple have been described. A mechanism for the reaction of metallic couples with water has been proposed.

It is concluded that the vectorial properties attending a given substance, by virtue of the mode of its formation, are largely responsible for the subsequent characterizations which that substance displays during the course of its chemical history.

The author wishes to thank Professor F. E. Bartell, in whose laboratory the experimental work described in this paper was carried out, for permission to publish these results.

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THE RÔLE OF ADSORPTION IN THE COAGULATION OF SOLS BY ELECTROLYTES¹

HARRY B. WEISER, W. O. MILLIGAN, AND W. J. COPPOC

Department of Chemistry, The Rice Institute, Houston, Texas

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The stability of sols of the hydrophobic type results from the adsorption of "potential-determining" ions (2) on the surface of highly dispersed particles. The adsorbed, potential-determining ions constitute the inner portion of a double layer, the outer portion of which is a diffuse layer of so-called counter ions. To illustrate: in the positively charged hydrous oxide sols prepared from the metallic chlorides by condensation methods, the inner portion of the double layer consists of the respective metallic ions and hydrogen, and the outer diffuse portion consists of the counter chloride ions. Similarly, in negative sols of the so-called "acidoid type," such as arsenic trisulfide, copper ferrocyanide, and silver iodide peptized by the respective acids, the anions of the acids are the potential-determining ions and hydrogen ions are the counter ions.

The coagulation of sols of the above-mentioned type by electrolytes results from the lowering of the electrokinetic or ζ -potential of the particles, which, in turn, is caused by contraction of the double layer or, if preferred, by compression of the outer layer surrounding the dispersed particles. This change in the double layer which reduces the ζ -potential has been attributed by the authors to adsorption of ions opposite in charge to the potential-determining ions which constitute the inner portion of the double layer. Since the adsorption of the added coagulation ions is greater than that of the counter ions of the diffuse outer layer, because of either the nature or the concentration of the added ions, the outer layer is compressed or the thickness of the double layer is reduced, thereby lowering the ζ -potential and reducing the stability of the sol. The adsorption, at least up to the coagulation point, is an exchange adsorption process in which the coagulating ions are in exchange with the counter ions of the diffuse outer layer. Some of the counter ions are held so strongly (adsorbed) by the attractive force of the inner layer that they are not a part of the intermicellar solution and therefore cannot be detected by potentiometric or electrometric methods in the original sol.

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The adsorption of the coagulating ions displaces these counter ions from the innermost portion of the outer layer and the displaced ions may be estimated subsequently in the intermicellar solution. The changes which are assumed to take place on adding coagulating electrolytes stepwise to sols (titrations of sols) are illustrated in figures 1 and 2.

Figure 1 gives the results of titrating two different hydrous oxide sols with potassium sulfate (8, 9, 10, 11). It will be noted that the coagu-

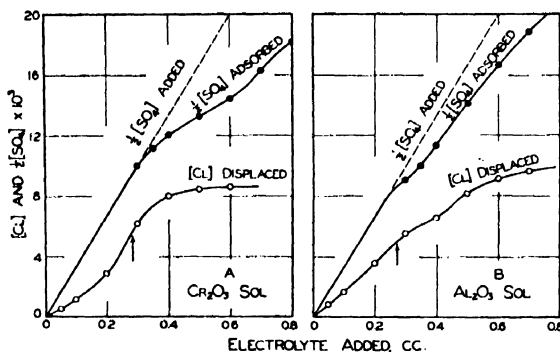


FIG. 1. Simultaneous displacement of chloride ion and adsorption of sulfate ion on titrating hydrous oxide sols with potassium sulfate.

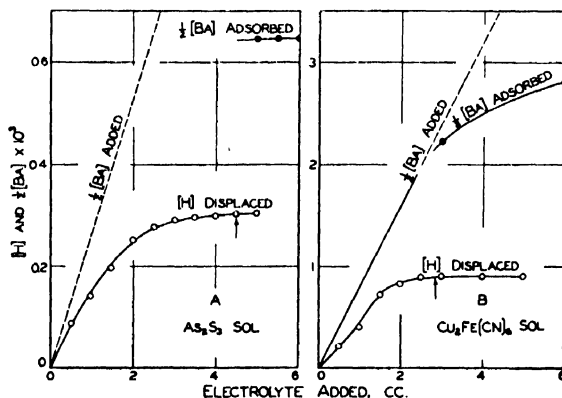


FIG. 2. Simultaneous displacement of hydrogen ion and adsorption of barium ion on titrating "acidoid" sols with barium chloride.

lating sulfate ion is adsorbed almost completely up to the precipitation value (indicated by an arrow), above which the adsorption curve is similar to that of the usual adsorption isotherm. The curve for the displacement of chloride from the innermost portion of the double layer falls well below that of the adsorption curve, since a part of the adsorbed sulfate ions replace the counter chloride ions which are so far out in the diffuse layer that they are a part of the intermicellar solution of the original sol.

Figure 2 (12, 13, 14) gives the results of titrating two sols of the acidoid

type with barium chloride. In these systems barium ions are adsorbed in exchange with hydrogen ions in the diffuse outer layer. The adsorbed barium ions displace hydrogen ions from the innermost portion of the outer layer, as shown in the curves for hydrogen displacement. Again, the adsorption of barium is much greater than the displacement of hydrogen, since a large part of the hydrogen replaced by barium in the outer layer was in the intermicellar solution originally. Unlike the behavior of the hydrous oxide sols shown graphically in figure 1, the displacement of counter ions from the innermost portion of the outer layer of the acidoid sols is practically complete at the precipitation concentration. The adsorption is also about complete at the precipitation value for arsenic trisulfide sol, whereas the adsorption has not attained its maximum value at the point of coagulation of the more highly gelatinous copper ferrocyanide sol.

Similar titration studies by Verwey and Kruyt (5,6) on silver iodide sol led to conclusions somewhat different from the above. In the sol employed hydriodic acid was the stabilizing electrolyte, hence it was a sol of the acidoid type like arsenic trisulfide and copper ferrocyanide. With the aged sols used by Verwey and Kruyt, the titration procedure was more complicated and less exact than with the sols employed by the authors. In the first place, the particle charge was much smaller in the iodide sols and the concentration of counter hydrogen ions was much smaller than in arsenic trisulfide and copper ferrocyanide sols of similar concentrations. Moreover practically all the counter ions were measurable potentiometrically in the original silver iodide sol; hence the amount of hydrogen displaced on adding electrolytes was inappreciable. The measurement of hydrogen ion exchanged for the added cation had to be determined in the ultrafiltrate after the addition of the coagulating electrolyte. This introduced errors which may be more or less serious depending on the conditions (4).

The procedure of Verwey and Kruyt was as follows: 15 to 25-cc. portions of sol were weighed in glass-stoppered flasks and varying amounts of electrolyte were added, followed by reweighing. After twenty-four hours the uncoagulated samples were ultrafiltered; the coagulated ones were centrifuged and the supernatant solution decanted. The exchanged hydrogen ion was determined colorimetrically or with the glass electrode. Since nearly all the hydrogen ions were in the intermicellar solution, the exchanged hydrogen may serve as an indirect measure of the amount of cation adsorbed. The adsorption of uranium and cerium was estimated colorimetrically. The results of some observations with a few different sols are shown graphically in figure 3.

From the form of the curves in figure 3, it appears that in certain instances the precipitation value (indicated by an arrow) occurs near the

point of maximum adsorption, in accordance with the authors' observations with arsenic trisulfide sol shown in figure 2. In other instances, however, the maximum adsorption by silver iodide appears to fall well below the precipitation concentration. From these and other observations Verwey and Kruyt conclude that adsorption is neither a necessary nor a sufficient cause of potential reduction at the surface of the particles; instead the potential reduction may result from compression of the outer layer without adsorption of the precipitating ions. In opposition to this point of view, all the observations of the authors indicate that the contraction of the double layer or the compression of the outer layer necessary to lower the potential to the coagulation point is the result of adsorption of the precipitating ions.

Since it is not obvious to us how one can have a stable coagulum if the precipitating ions are not carried down (adsorbed) by the agglomerated

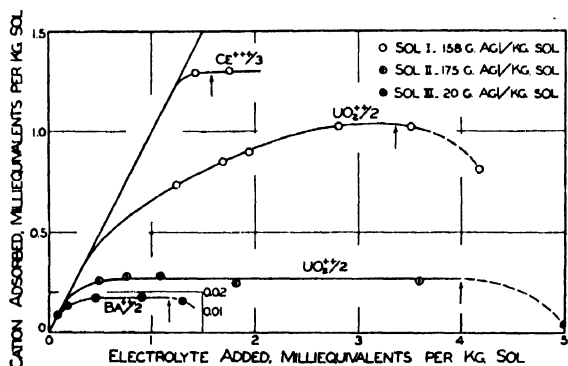


FIG. 3. Adsorption of cations on titrating silver iodide sols with electrolytes (after Verwey and Kruyt).

particles, some of the observations of Verwey and Kruyt would seem to call for special consideration. As already pointed out, the behavior of sol I (figure 3) with certain cations, e.g., UO_2^{++} and Ce^{+++} , is similar in all essential respects to that of the acidoid arsenic trisulfide (figure 2) and sulfur sols with various cations. The barium adsorption estimated indirectly from pH measurements on the ultrafiltrate from sol III (figure 3) can be disregarded, since the change in hydrogen-ion concentration is too small to measure accurately. The behavior of sol II with UO_2^{++} cannot be disposed of in this way. But the fact that the adsorption of UO_2^{++} and Ce^{+++} reaches a maximum near the coagulation point of the respective ions for sol I, whereas the adsorption of UO_2^{++} appears to attain a maximum value well below the coagulation concentration of sol II, calls for an explanation. One possibility is that the stability of sol II results in part from the presence of a stabilizing impurity derived from the membrane used in the dialysis. If such contamination is ruled out, another

possibility is that the size distribution of the particles in sol II is quite different from that in sol I. If most of sol II is coagulated at low concentrations but the last trace only at relatively high concentrations (taken as the precipitation value), and if sol I does not exhibit such marked stepwise coagulation, the difference in the behavior of the two sols toward UO_2^{++} may be accounted for. The following experiments indicate that the usual definition of the precipitation value for sols that are quite polydisperse may be unsatisfactory, provided the precipitation value is compared with some other property of the system.

THE STEPWISE COAGULATION OF POLYDISPERSE SOLS

Silver iodide sols

Concentrated silver iodide sols were prepared as follows: Solutions of silver nitrate and hydrogen iodide were made up approximately 0.20 and 0.22 *N*, respectively, and titrated against each other by neutralizing the acid with excess calcium carbonate and taking the end point with potassium chromate as indicator. The required amounts of the two solutions cooled to 0°C. were mixed in a quick-mixing apparatus to give about 500 cc. of a sol containing 100 millimoles of silver iodide per liter with 10 per cent excess of the stabilizing iodide ion. The resulting sol was transferred to an electrodialysis apparatus and electrodialyzed for forty-eight hours at 700 volts and 10 to 20 milliamperes. The dialysis membranes were of Cellophane which had been previously soaked in 63 per cent zinc chloride (3) and thoroughly washed. After the dialysis the relatively pure sol was evaporated at room temperature to 100 cc. by passing a current of cleaned, dried air over it. The resulting preparation was quite stable, had a pH value of 3.5 to 3.7, and contained approximately 60 g. of silver iodide per liter. Several portions prepared simultaneously were mixed to give the sol used in the subsequent precipitation experiments. Two preparations made at different times were employed.

In the precipitation experiments 15 cc. of sol and 5 cc. of electrolyte of the concentration desired were mixed in a small, all-glass, quick-mixing apparatus. The resulting mixture was transferred to a Pyrex test tube and allowed to stand for eighteen hours, after which it was shaken again for ten seconds to break up a kind of gel-like structure which may form during slow coagulation (7). At the end of twenty-four hours, a 5-cc. sample was pipetted from the top of the solution and analyzed for silver iodide. This was accomplished by coagulating the sol with barium chloride, filtering through a Gooch crucible, washing with 0.25 per cent nitric acid until the washings gave no precipitate with sulfuric acid, drying overnight at 110°C., and weighing. Experiments were carried out with the chlorides of potassium, barium, calcium, and aluminum and with lanthanum nitrate and calcium sulfate. Some typical results given in

figures 4 and 5 show that (a) the polydisperse sols undergo stepwise coagulation, (b) most of the sol is coagulated in a rather narrow range, and (c) the usual precipitation value, i.e., the point of complete coagulation, indicated by an arrow, may be a concentration 50 to 100 per cent above the concentration required to precipitate 95 per cent of the sol.

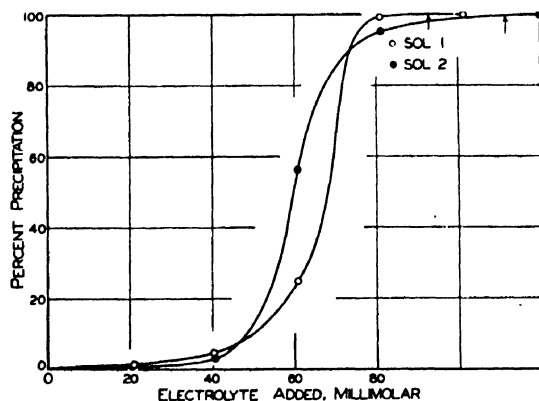


FIG. 4. The stepwise coagulation of silver iodide sols with potassium chloride. Arrows indicate the points of complete coagulation.

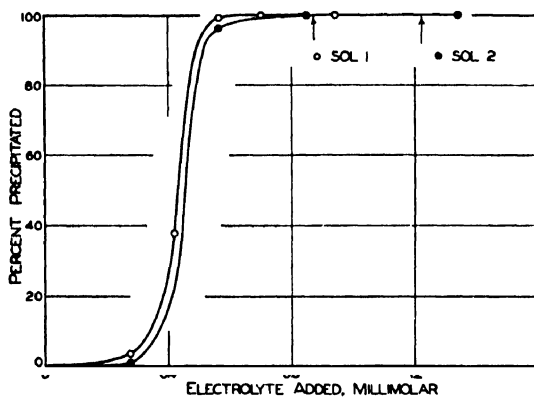


FIG. 5. The stepwise coagulation of silver iodide sols with barium chloride. Arrows indicate the points of complete coagulation.

Arsenic trisulfide sols

Two sols were prepared by two different methods of procedure. The first method, described by Freundlich and Nathansohn (1), is as follows: To 100 cc. of a saturated solution of arsenic trioxide was added 100 cc. of a solution of hydrogen sulfide containing 1 cc. of a saturated solution of the gas. The resulting yellowish mixture was diluted to 1 liter with hydrogen sulfide water ten times as strong as the above. The mixture was then saturated with hydrogen sulfide gas, after which the excess was

washed out with a current of hydrogen. By adding very dilute hydrogen sulfide at the start, nuclei are formed throughout the solution; this favors the formation of a monodisperse sol. The concentration was 2.51 g. of arsenic trisulfide per liter.

A second sol of similar concentration was prepared by conducting hydrogen sulfide into 100 cc. of saturated arsenic trioxide, diluting to 1 liter, saturating with hydrogen sulfide, and washing out the excess with a current of hydrogen. This procedure would tend to give a more polydisperse sol than Freundlich and Nathansohn's method.

The precipitation experiments were carried out in much the same way as with the silver iodide sol, except that 20 cc. of the sol was mixed with 5 cc. of electrolyte, and after twenty-four hours a 10-cc. sample was taken for analysis. The results with potassium chloride as precipitating electrolyte are shown graphically in figure 6. The experiments show

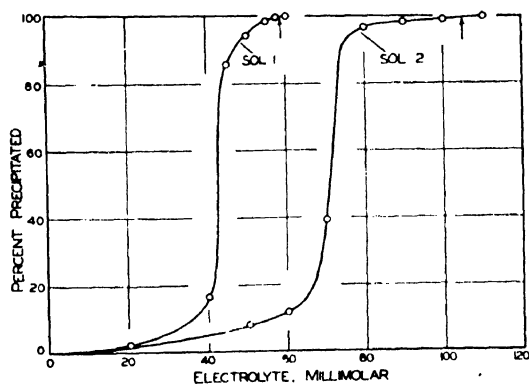


FIG. 6. The stepwise coagulation of arsenic trisulfide sols with potassium chloride. Arrows indicate the points of complete coagulation.

that Freundlich and Nathansohn's sol is less polydisperse than that formed by conducting hydrogen sulfide directly into saturated arsenious oxide solution. The point of complete precipitation (precipitation value) of the Freundlich and Nathansohn sol is but 20 per cent above the point where 95 per cent of the sol is coagulated, whereas the precipitation value of the more polydisperse sol is 40 per cent above the concentration required to coagulate 95 per cent of the sol.

The precipitation value of an electrolyte for a sol is ordinarily taken as that concentration which will cause complete coagulation in a definite time. It is apparent from the above experiments that for polydisperse sols the precipitation value, as defined above, may fall well above the concentration required to precipitate most of the sol. It would seem to be permissible to compare the precipitation values of various electrolytes for a given polydisperse sol among themselves. But if the point of com-

plete coagulation is well above the concentration required for precipitating a large percentage of the sol, the point of maximum adsorption may fall well below the precipitation value as usually defined. This may be in part responsible for Kruyt and Verwey's observation that the precipitation value for certain silver iodide sols falls well above the point of maximum adsorption of the precipitating ion.

SUMMARY AND CONCLUSIONS

1. The coagulation of hydrophobic sols by electrolytes results from the lowering of the electrokinetic or ζ -potential of the particle which, in turn, is caused by contraction of the double layer or, if preferred, by compression of the outer layer surrounding the dispersed particles. This change in the double layer, which reduces the ζ -potential, is attributed to adsorption of precipitating ions opposite in charge to the potential-determining ions which constitute the inner portion of the double layer.

2. In the coagulation of sols of the hydrous oxides of iron, aluminum, and chromium, and of the "acidoid" sols of arsenic trisulfide, sulfur, and copper ferrocyanide, practically complete coagulation by electrolytes takes place at or below the point of maximum adsorption of the precipitation ion.

3. With certain sols of silver iodide Verwey and Kruyt observed that the precipitation value of certain electrolytes was well above the point of maximum adsorption. From these and other observations it was concluded that adsorption is neither a necessary nor a sufficient cause of potential reduction at the surface of the particle.

4. An attempt has been made to account for the apparently anomalous behavior of certain silver iodide sols as observed by Verwey and Kruyt.

5. For highly polydisperse sols the concentration of electrolyte required for complete coagulation in a given time (the precipitation value) may fall well above the concentration necessary to precipitate a large percentage of the sol.

6. If the point of complete coagulation in a polydisperse silver iodide sol is well above the concentration required for precipitating a large percentage of the sol, the point of maximum adsorption may fall well below the precipitation value as usually defined. It is suggested that this may account, in part, for Kruyt and Verwey's observation noted in paragraph 3 above.

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THE SYSTEM NICKEL SULFATE-SULFURIC ACID-WATER AT 25°C. AND 0°C.

J. A. ADDLESTONE

Department of Chemistry, Virginia Polytechnic Institute, Blacksburg, Virginia

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The system nickel sulfate-sulfuric acid-water has been studied by Montemartini and Losana (1), who give data for the 12.5°C. isotherm. Rohmer (2) has investigated this system at 25°C. and 50°C., and gives data for the various transition points of the hydrates of nickel sulfate. This study was undertaken with the purpose of obtaining the complete isotherms for this system at 25°C. and 0°C.

EXPERIMENTAL PROCEDURE

A series of solutions containing approximately 100 cc. of varying concentrations of sulfuric acid were saturated with nickel sulfate. For the lower acid concentrations the solutions were saturated with the hexahydrate, and in the higher acid concentrations the solutions were saturated with anhydrous nickel sulfate. For the 25°C. isotherm these solutions were placed in a constant-temperature water bath. For the 0°C. isotherm the bottles were placed in a large container packed with finely divided ice. The temperature range varied from approximately 0°C. to 0.2°C.

The bottles were shaken by hand at least three times a day and allowed to remain in the bath for four weeks. The solutions were then allowed to settle and samples of the clear liquid were taken for analysis. Solid phases were removed for analysis by means of a glass spoon, as much of the liquid phase as possible being allowed to drain off.

Nickel was determined gravimetrically by the usual dimethylglyoxime method, and sulfate was determined by precipitation with barium chloride. The nickel was calculated to nickel sulfate, and the excess sulfate was calculated to sulfuric acid. Water was determined by difference.

The composition of the solid phases in equilibrium with the various solutions was determined graphically by means of intersecting tie-lines.

The analyses of the liquid and solid phases are given in weight per cent of NiSO_4 , H_2SO_4 , and H_2O .

RESULTS AND DISCUSSION •

The data for the 25°C. isotherm are given in table 1 and the results are plotted in figure 1. Data for the 0°C. isotherm are given in table 2 and plotted in figure 2.

TABLE 1
25°C. isotherm

LIQUID PHASE			WET RESIDUES			COMPOSITION OF SOLID PHASE
NiSO ₄	H ₂ SO ₄	H ₂ O	NiSO ₄	H ₂ SO ₄	H ₂ O	
weight per cent	weight per cent	weight per cent	weight per cent	weight per cent	weight per cent	
28.13		71.87				NiSO ₄ ·7H ₂ O
27.34	1.79	70.87	48.07	0.63	51.30	
27.16	3.86	68.98	53.32	0.23	46.45	
26.15	4.92	68.93	53.62	0.85	45.53	NiSO ₄ ·6H ₂ O
23.71	6.85	69.44	52.60	1.27	46.13	
22.26	7.93	69.81	57.02	0.47	42.51	
16.51	16.52	66.97				
15.64	19.34	65.02				
11.23	34.48	54.29	55.95	1.96	42.09	
10.56	44.68	44.76	55.63	2.14	42.23	
12.80	45.12	42.08	57.84	9.55	32.61	NiSO ₄ ·6H ₂ O and NiSO ₄ ·H ₂ O
9.65	48.46	41.89	68.74	12.63	18.63	NiSO ₄ ·H ₂ O
4.59	58.53	36.88	73.36	11.40	15.24	
2.67	63.73	33.60				
0.23	72.38	27.39				
0.15	84.52	15.33	43.40	44.27	12.33	
0.12	91.38	8.50	26.02	64.36	9.62	
0.11	93.74	6.15	24.20	71.29	4.51	NiSO ₄
0.08	96.80	3.12	21.58	76.14	2.28	

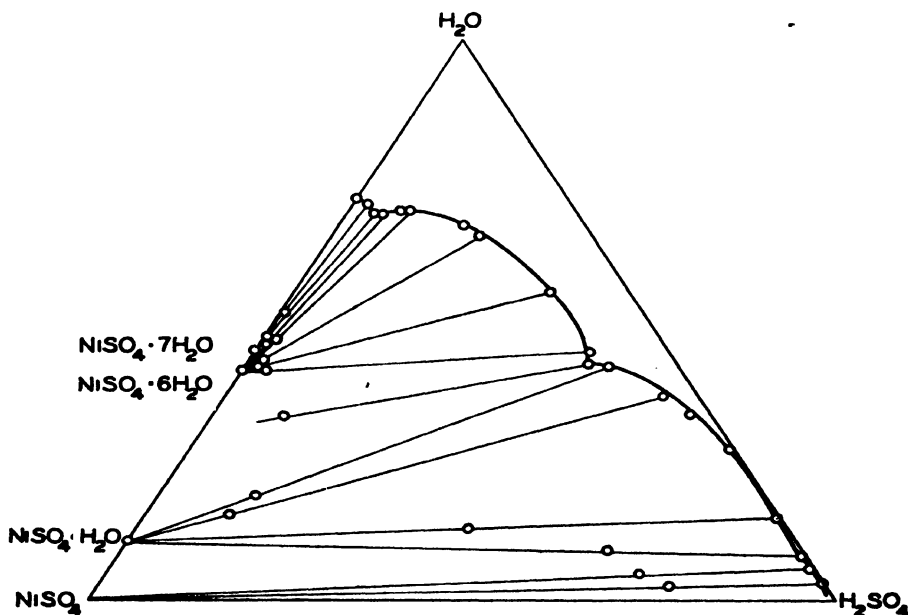


FIG. 1. Plot of the data for the 25°C. isotherm

TABLE 2
0°C. isotherm

LIQUID PHASE			WET RESIDUES			COMPOSITION OF SOLID PHASE
NiSO ₄	H ₂ SO ₄	H ₂ O	NiSO ₄	H ₂ SO ₄	H ₂ O	
weight per cent	weight per cent	weight per cent	weight per cent	weight per cent	weight per cent	
21.17		78.83				NiSO ₄ ·7H ₂ O
19.22	2.63	78.15				
13.86	10.06	76.08	47.67	1.74	50.59	
9.41	18.36	72.23	51.08	1.81	47.11	
9.22	22.64	68.14	49.08	2.96	47.96	
8.58	25.05	66.37	53.04	2.45	44.51	NiSO ₄ ·6H ₂ O
5.06	30.10	64.84	54.74	1.92	43.34	
2.62	42.88	54.50	49.25	7.27	43.48	
4.68	50.72	44.60	51.36	6.28	42.36	
5.42	52.88	42.30	51.10	15.83	33.07	NiSO ₄ ·6H ₂ O and NiSO ₄ ·H ₂ O
4.15	58.12	37.73	39.63	33.30	27.07	NiSO ₄ ·H ₂ O
3.71	60.11	36.18				
0.24	75.19	24.57				
0.18	79.83	19.99	Trace	82.12	17.88	H ₂ SO ₄ ·H ₂ O and NiSO ₄ ·H ₂ O
0.11	86.67	13.22	Trace	59.44	14.32	
				84.96	15.04	
0.09	90.82	9.09	32.33	57.96	9.71	NiSO ₄ ·H ₂ O
0.07	94.25	5.68	41.85	49.95	8.19	
0.06	97.19	2.75	24.58	69.13	5.29	

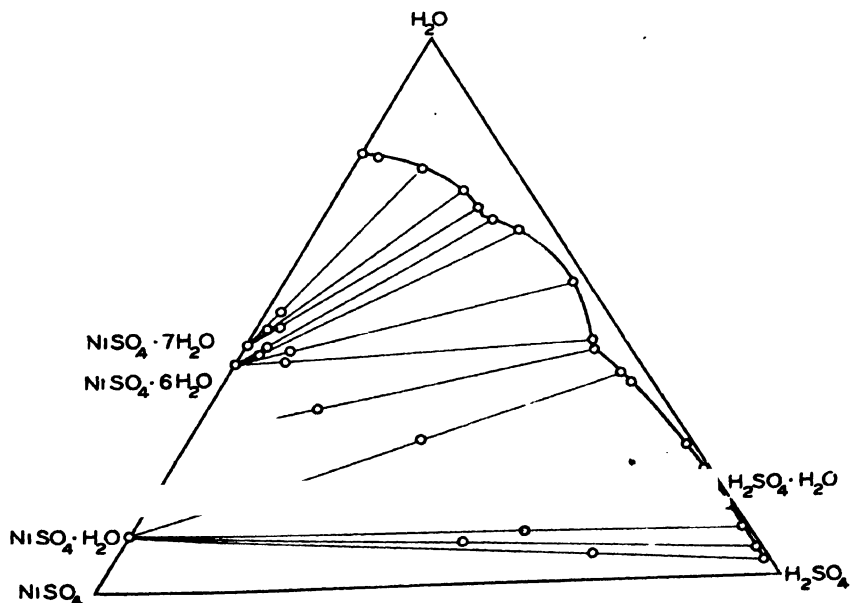


FIG. 2. Plot of the data for the 0°C. isotherm

At 25°C. the solubility of the various hydrates decreases with increasing sulfuric acid concentration. The solubility decreases rapidly at about 60 per cent sulfuric acid. The stable solid phases at 25°C. are the heptahydrate, the hexahydrate, the monohydrate, and anhydrous nickel sulfate. Evidence of a metastable tetrahydrate of nickel sulfate was found between approximately 45 per cent and 50 per cent sulfuric acid. These solid phases agree with those reported by Rohmer (2).

The solubility curves at 0°C. exhibit the same general shape as those at 25°C. The stable solid phases at 0°C. are the heptahydrate, the hexahydrate, and the monohydrate of nickel sulfate. The monohydrate of sulfuric acid also exists as a stable solid phase at this temperature. Anhydrous nickel sulfate, which was found at 25°C. and reported by Montemartini and Losana (1) to be present at 12.5°C., was not found at 0°C. The dihydrate of nickel sulfate was not present at 0°C., although Montemartini and Losana (1) found this hydrate to be stable at 12.5°C.

SUMMARY

The 25°C. and 0°C. isotherms for the system nickel sulfate-sulfuric acid-water have been determined.

The stable solid phases at 25°C. are $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$, $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$, $\text{NiSO}_4 \cdot \text{H}_2\text{O}$, and NiSO_4 . $\text{NiSO}_4 \cdot 4\text{H}_2\text{O}$ exists as a metastable phase.

The stable solid phases at 0°C. are $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$, $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$, $\text{NiSO}_4 \cdot \text{H}_2\text{O}$, and $\text{H}_2\text{SO}_4 \cdot \text{H}_2\text{O}$.

The author is grateful to Dr. H. D. Crockford for suggestions concerning this work.

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LUMINESCENCE AND COLOR EXCITED BY RADIUM IN ZINC BORATE GLASSES WHICH CONTAIN MANGANESE

BYRON E. COHN

Department of Physics, University of Denver, Denver, Colorado

AND

S. C. LIND

School of Chemistry, University of Minnesota, Minneapolis, Minnesota

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INTRODUCTION

It is well known that radiations from radium color certain soda-silicate glasses a deep violet color. Rutherford (9) attributes to M. and Mme. Curie the first observations of this effect. Clarke (1) found that glasses colored purple by exposure to radium contained manganese, whereas the purple color was not produced in the absence of manganese. As early as 1901 Wiedemann (10) showed that certain solids when exposed to radium exhibited the property of thermoluminescence. Because exposure to radium produces both coloration and thermoluminescence and because heat discharges both the luminescence and the color, these effects have been associated by many of the workers in this field. However, on the basis that the thermoluminescence could be liberated without markedly changing the visible color, Lind (6) indicated that the connection between color and luminescence was not always so close as had commonly been supposed. An investigation of the effects of exposure to radium of synthetic zinc borate glasses, each of which contained a known concentration of manganese, offered promise of more exact information than has hitherto been available. This paper is the report of such an investigation.

THERMOLUMINESCENCE

A series of zinc borate glasses in the form of 6-mm. squares, each 2.7 mm. thick, which contained known amounts of manganese ranging between 0 and 5 per cent were prepared as indicated by Cohn and Harkins (3). These samples were exposed to 140 mg. of radium at a distance of 1.7 cm. for the equivalent of approximately seven gram-days.¹ Under the conditions of exposure the radiation responsible for the energizing of the

¹ Exposure to 1 g. of radium for one day is referred to as a gram-day; if a glass were exposed to 0.1 g. for ten days, this also would be indicated as one gram-day.

glass specimens was mainly gamma rays, although beta radiation may have contributed a small fraction of the energy. The thermoluminescence was determined by a modification of the total light area method of Nyswander and Lind (8). Intensity-time areas of glass samples heated at a constant temperature of 100°C. were taken as a measure of the energy emitted in the process of luminescence. The values of the areas were then each multiplied by the same factor, so that the maximum luminescence would have the value 100. The results are presented in figure 1, curve A. The values of manganese concentration are plotted on a non-uniform scale in order to spread the values for the lower concentrations, as the greatest changes were in this region. Semilogarithmic cross-section paper was used for this purpose. From this graph it can be seen that a change in the amount of manganese in a glass specimen has an effect which is quite

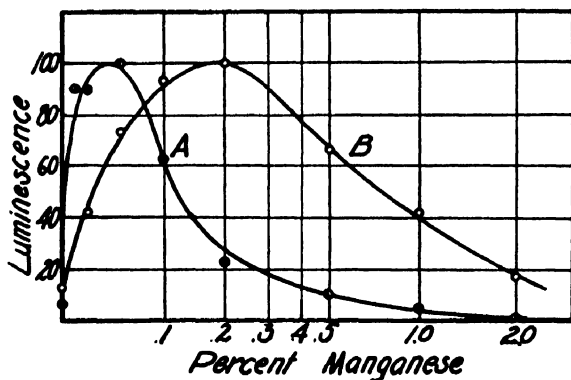


FIG. 1. Thermoluminescence in zinc borate glasses which contain manganese. Curve A, thermoluminescence excited by exposure to radium; curve B, thermoluminescence excited by exposure to quartz mercury arc.

similar to the effect of activators when other sources of energy are used to excite the luminescence. It will be observed that the optimum concentration of manganese is approximately 0.05 per cent. To determine the effect of the time of exposure to radium upon the optimum concentration the luminescence was measured in a set of samples whose exposure to radium was equivalent to approximately 120 gram-days at a distance of 1.7 cm. This time the maximum intensity method of Nyswander and Cohn (7) was employed. It was found that the optimum concentration remained at 0.05 per cent, manganese. The optimum concentration is therefore independent of time of exposure. This is of considerable interest, as is evident from the comparison of curves A and B in figure 1. Curve B presents the values for the thermoluminescence excited by ultraviolet light (mercury arc in quartz) and was obtained by Cohn and Harkins (3). It can be seen that the optimum concentration for the thermoluminescence

is approximately 0.2 per cent in the latter case. A possible reason for the shift of the optimum will be indicated later in this paper.

The emission spectrum of the luminescence induced in these zinc borate glasses is a band in the red, yellow, and green with its maximum intensity in the red at about 6000 Å. The spectrum was examined visually with the aid of a transmission grating, using the edge of a glowing specimen as its own slit. The emission spectrum appears the same whether radium or ultraviolet light is used to excite the thermoluminescence. Indeed, the spectrum emitted appears to be independent of the means of excitation or of the type of luminescence (fluorescence or thermoluminescence). Similar emission in the type of glasses used was found by Cohn (2) for ultraviolet fluorescence, and by Kabakjian (5) in the case of cathode-ray fluorescence. Both workers used zinc borate glasses which contained manganese.

COLOR PRODUCED BY EXPOSURE TO RADIUM

A series of zinc borate glasses as indicated in the preceding section were exposed to radium. Before irradiation the glass squares appear colorless when they contain less than 1 per cent of manganese. They have a very slight yellowish tint beginning at 1 per cent of manganese and increasing in intensity for samples up to 3 per cent of manganese. Samples which contained 4 and 5 per cent of manganese are a light amber color. Upon exposure to radium the samples which contain manganese acquire a violet-purple tint of much smaller intensity than is the case in soda lime glasses. The sample which contained the highest concentration of manganese acquired the violet-purple tint first, and so on in the order of manganese content. After exposure at a distance of 1.7 cm. for the equivalent of approximately seven gram-days the specimen which contained 0 per cent of manganese appeared slightly yellow; the 0.01 per cent manganese glass was of neutral gray tint; the 0.02 per cent sample exhibited a trace of blue-violet, which tint appeared to increase in intensity with increase of manganese concentration to samples which contained 0.2 per cent manganese. The samples which contained more than 0.2 per cent manganese exhibited about the same intensity of coloration. However, the color tint in specimens which contained more than 1 per cent of manganese was of pink-violet hue as opposed to the blue-violet color of the others. It was found that the color change appeared to approach a maximum value for a given concentration of manganese. For example, the change in the visible absorption determined in samples exposed approximately 120 equivalent gram-days at a distance of 1.7 cm. was almost the same as for glasses exposed 7 gram-days at the same distance. The small difference in the absorption in these glasses after a strong exposure agrees with a similar finding by Kabakjian (4), who found that the coloring due

to exposure to radium approached a constant value provided the intensity of the source remained constant.

LIGHT ABSORPTION IN THE ULTRAVIOLET REGION

Spectra were photographed of the transmission of the lines from a quartz mercury arc through the original samples as compared with samples which had been exposed to radium. This was done by placing the glass squares one above the other in front of the slit of a Gaertner quartz prism spectrograph, and photographing the resulting spectrum. Figure 2 shows a set of the comparison spectra for a zinc borate glass which contained 0.1 per cent of

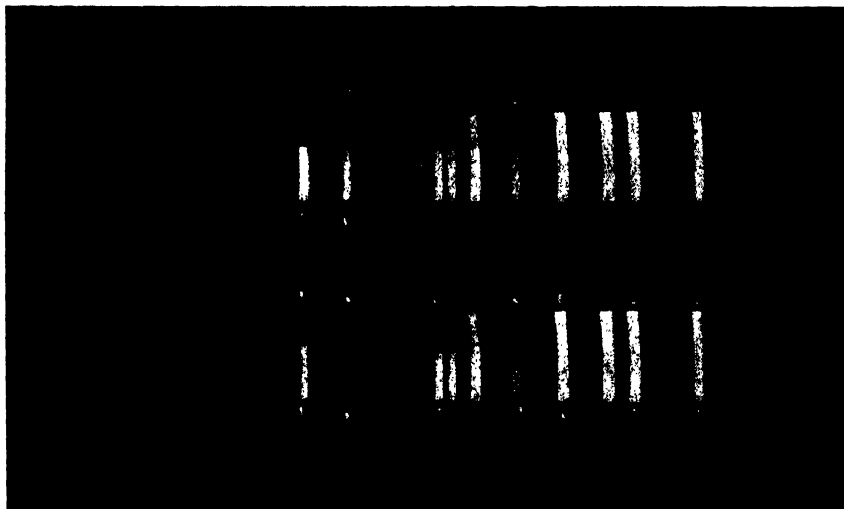


FIG. 2. Comparison spectra through zinc borate glass which contains 0.1 per cent of manganese. Upper spectrogram: top, through 2.7 mm. of glass exposed to radium; bottom, mercury arc lines. Lower spectrogram: top, through 2.7 mm. of glass exposed to radium; bottom, through 2.7 mm. of same glass not exposed to radium.

manganese. The upper spectrogram presents (upper half) the spectrum of a quartz mercury arc when the light was caused to pass through 2.7 mm. of zinc borate glass which had been exposed to radium. The lower half of the upper spectrogram shows the mercury spectrum as received upon the slit of the spectrograph. The lower spectrogram presents a direct comparison between a zinc borate glass which had been exposed to radium (upper half) as compared with a zinc borate glass of the same thickness which had not previously been exposed to radium (lower half). The concentration of manganese in both glasses was 0.1 per cent. From the lower spectrogram it is evident that exposure of the glass to radium produced a striking change in its transmission for shorter wave lengths of light.

Quantitative measurements of the change in transmission in the ultra-violet region were made. The measurement of the density of the photographic deposit caused by ultraviolet light passing through (a) glasses which had not previously been exposed to radium and (b) glasses of the same manganese content which had previously been exposed to radium were made with the aid of a densitometer arranged for the purpose. The photographic plates were Eastman D.C. Orthochromatic and were developed by Rodinal (1 part) and water (15 parts) for 4 minutes at 20°C. using rocked-tray technique. They were placed for 45 minutes in a fixing

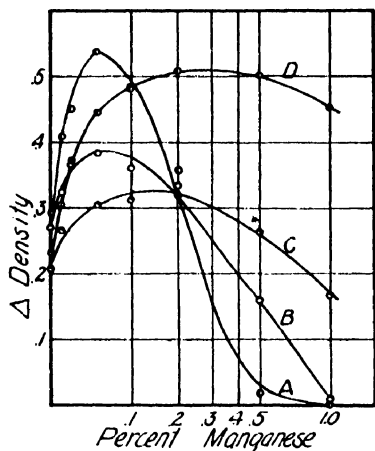


FIG. 3

FIG. 3. Change in absorption caused by exposure to radium. The absorption is indicated as density changes at given wave lengths as a function of the concentration of manganese. Curve A, 2537 Å.; curve B, 2654 Å.; curve C, 2804 Å.; curve D, 2967 Å.

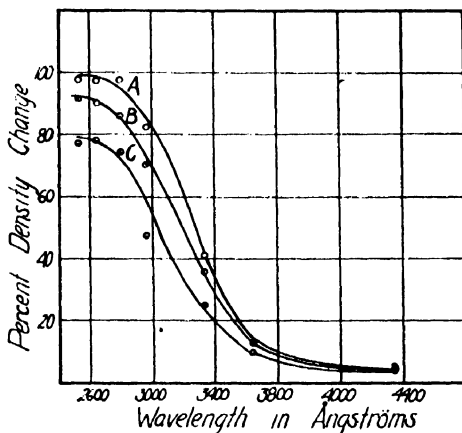


FIG. 4

FIG. 4. Per cent absorption change caused by exposure to radium. The absorption is indicated as per cent density change graphed as a function of wave length. Curve A, 0.2 per cent manganese; curve B, 0.05 per cent manganese; curve C, 0.01 per cent manganese.

bath at 20°C., and then were thoroughly washed and dried in a dust-free atmosphere. The densitometer consisted of a light source, a microscope, a photronic cell equipped with a slit, and a galvanometer. The image of the spectrum line on the photographic plate was thrown upon the slit of the photronic cell, and the light intensity was recorded by means of the galvanometer. The intensity of the light source was held constant by means of a voltage regulator. The densities of the deposits on the photographic plate were computed, and the curves for the changes in density due to the exposure of the glasses to radium were determined. The photographic density (D) for each spectrum line was computed by the formula

$$D = \log_{10} G_0/G$$

where G_0 was the value of the galvanometer deflection given by the projection of light through the clear plate in the vicinity of the spectrum line, and G was the galvanometer deflection when the image of the spectrum line covered the slit aperture of the photronic cell. The change in density was expressed as the difference $D_N - D_R$, where D_N was the density of the spectrum line obtained by passage of the light through the original glass and D_R was its density after passage through a glass which had been exposed to radium.²

In figure 3 are presented curves which show the change in density ($D_N - D_R$) due to exposure to radium plotted as a function of the concentration of manganese. Curve A represents the change in absorption at

² The approximate relationship between the values of the change in density (ΔD) computed from the measurements on a photographic plate with the value of the change in extinction coefficient (ΔE) which could be obtained from direct measurement is indicated in the following. By definition the extinction coefficient (E) is given by

$$E = 1/d \log_{10} I_0/I$$

where I_0 is the light transmitted initially, I is the intensity transmitted through the specimen, and d is the thickness of the specimen. If measurements were made with two specimens, one exposed to radium giving a transmitted intensity I_R , the second of the same original material but not exposed to radium, giving a transmitted intensity I_N , and with the same light intensity from a monochromator, I_0 , one would obtain

$$\Delta E = E_R - E_N = \left(\frac{1}{d} \log_{10} I_0/I_R \right) - \left(\frac{1}{d} \log_{10} I_0/I_N \right)$$

or

$$\Delta E = \frac{1}{d} (\log_{10} I_N/I_R)$$

Assuming (1) the Abney-Schwarzschild law of the photographic plate,

$$D = \gamma \log_{10} I t^p - i$$

(2) a fixed time of exposure, and (3) a constant developmental procedure, one obtains for (ΔD) from this equation

$$\Delta D = D_N - D_R = \gamma \log_{10} I_N/I_R$$

From the definition for D above in terms of galvanometer deflections and the assumption of the direct proportionality of galvanometer deflection to light at the slit of the photronic cell, one obtains

$$\Delta D = \log_{10} G_R/G_N = \gamma \log_{10} I_N/I_R$$

From these two values one obtains for ΔE the result

$$\Delta E = \frac{1}{d\gamma} \log_{10} G_R/G_N = \frac{1}{d\gamma} \Delta D$$

The change in extinction coefficient is therefore approximately equal to the change in density divided by the product of the thickness of the sample and the photographic constant gamma.

2537 Å., curve B at 2654 Å., curve C at 2804 Å., and curve D at 2967 Å. A progressive shift of the maximum absorption toward higher manganese concentration with increasing wave length is quite apparent. It will be noted that the exposure to radium has caused the appearance of an absorption band in the ultraviolet region of the spectrum; that for the region in the vicinity of 2500 Å. the absorption band has its maximum concentration at approximately 0.05 per cent manganese, but that at longer wave lengths this absorption band is displaced toward a higher concentration of manganese. At 2967 Å. the maximum of the absorption band corresponds approximately to 0.3 per cent manganese. From this it would seem that the optimum concentration for the thermoluminescence is very closely related to this absorption in the ultraviolet region, as a similar shift in the optimum thermoluminescence was observed in figure 1. It is readily understood that the optimum condition for luminescence will be at that concentration where conditions are most favorable for the production of that luminescence. If the luminescence due to radium is an optimum at 0.05 per cent manganese, it means that the conditions are most favorable when the ratio of zinc to manganese atoms in the zinc borate glass has a given value. Since the optimum for thermoluminescence induced by exposure to radium closely approximates a change of absorption in the region of 2500 Å., it is probable that the particular reaction between material and light which produces luminescence is directly related to the absorption in the ultraviolet region.

It is of some interest to obtain the approximate form of the absorption curve as a function of the wave length. To do this the values of the changes in density similar to those presented in figure 3 were divided by the corresponding initial density for each concentration and spectrum line. These values were graphed as a function of wave length. Curve A of figure 4 gives the values of the per cent density change due to exposure to radium for zinc borate glasses which contain 0.2 per cent of manganese. Curve B presents the same relation for samples which contain 0.05 per cent of manganese, whereas curve C presents the values for samples which contain 0.01 per cent of manganese. This curve can be taken only as an approximate indication of the absorption, owing to the fact that a variation of the value of the photographic constant gamma with change of wave length is to be expected.

An even more striking fact is brought out when the difference in densities is again determined after the samples have been heated to discharge the luminescence. This was done by heating the samples for one hour at 135°C. Most of the luminescence is discharged by this process, although a small portion of energy available as luminescence may still remain. These values of change in density are subtracted from the original change in density to give a measure of the difference in the absorption which was

caused by the process discharging the luminescence. The process of obtaining these data is illustrated by figure 5. The change in density for wave length 2537 Å. before heating is presented in curve A. The difference of density after heating is indicated in curve B. The difference between the densities in curve A and curve B represents the change in absorption which occurred during the interval the luminescence was emitted, and is represented by curve C. The similarity in the shapes of each of these curves is apparent and appears to indicate the diminution in intensity of an absorption band. In figure 6 are graphed the changes in

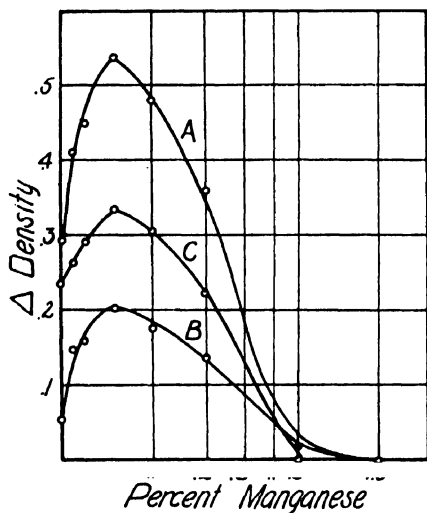


FIG. 5

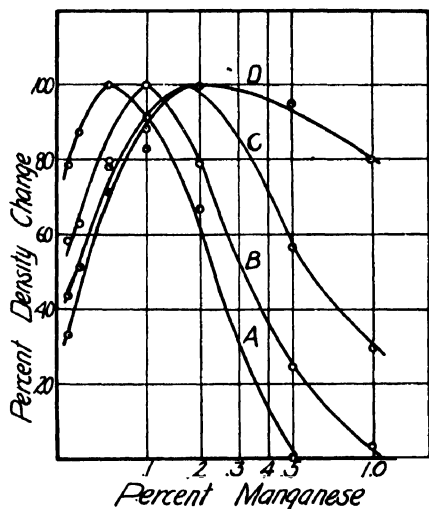


FIG. 6

FIG. 5. Absorption change during luminescence emission. The curves are all given for absorption changes at 2537 Å. Curve A, absorption caused by exposure to radium; curve B, absorption which remains after the emission of thermoluminescence; curve C, change in the absorption during the interval thermoluminescence was emitted.

FIG. 6. Change in absorption during the emission of luminescence. Curve A, 2537 Å.; curve B, 2654 Å.; curve C, 2804 Å.; curve D, 2967 Å.

density during the emission of luminescence for wave lengths 2537 Å. (curve A), 2654 Å. (curve B), 2804 Å. (curve C), and 2967 Å. (curve D). The maximum density for each wave length is given a value of 100 for the purpose of comparison, and therefore the ordinates are indicated as percent density change. This has been done to eliminate the intrinsic difference of the intensity of the mercury spectrum lines from the comparison. The change of absorption maximum with the wave length is quite evident.

In figure 7 curve A represents the change in absorption density at the wave length 2537 Å. during the time luminescence was emitted, whereas

curve B represents the luminescence which had its origin in the excitation due to exposure to radium. The densities and the luminescence have both been computed in such a way that an arbitrary value of 100 represents the maximum value of either curve. A similarity between the two curves is apparent. In figure 8 curve A represents the change in absorption at 2804 Å., while curve B represents the luminescence emitted when the luminescence is excited by ultraviolet light (see figure 1). The correspondence is again quite evident. From these results it appears that changes in the optimum concentration can be caused by the variation of the absorption of the exciting energy with wave length. It can be predicted that

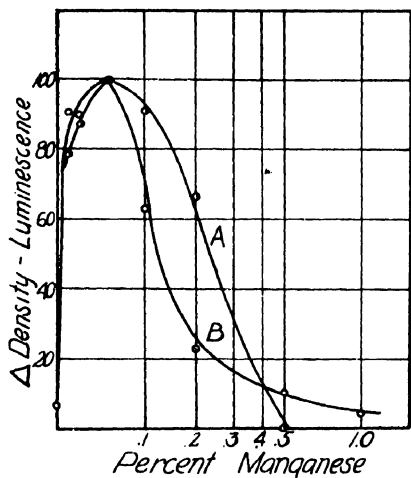


FIG. 7

FIG. 7. Comparison curves of absorption change and luminescence. Curve A, absorption change at 2537 Å. (figure 6, curve A); curve B, luminescence emitted due to radium (figure 1, curve A).

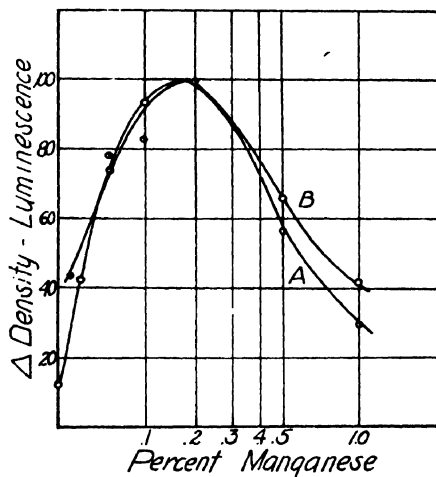


FIG. 8

FIG. 8. Comparison curves of absorption change and luminescence. Curve A, absorption change at 2804 Å. (figure 6, curve C); curve B, luminescence emitted, excited by mercury arc (figure 1, curve B).

a change in the wave length of an ultraviolet source used for the purpose of excitation of thermoluminescence would shift the optimum concentration for an activator.

LIGHT ABSORPTION IN THE VISIBLE REGION

It has been indicated that there appears to be a definite correspondence between the absorption changes in the ultraviolet region and the luminescence which is emitted from zinc borate glasses which contain manganese as an activator. It was desirable also to investigate quantitatively the changes in the visible transmission of these samples. Unfortunately, the change in the visible transmission was so small that photographic measurements could not give the necessary accuracy for the determination of the

difference in density. For this reason a direct measurement of the transmission of light confined to given spectrum regions was obtained by means of filters. The densitometer used consisted of a light source, filter, lens, aperture, photronic cell, and galvanometer. The light source was a 40-watt tungsten-filament lamp which was supplied with current from the secondary of a regulating transformer. During the measurements the voltage across the lamp remained at 112.4 volts ± 0.1 volt. The density (D) for each sample was computed from the photometric measurement by

$$D = \log_{10} I_0/I$$

where I_0 is the galvanometer reading corresponding to the initial intensity and I is the galvanometer reading after the light has traversed the sample. The values for the changes in density are given by $D_R - D_N$, where D_R is the value of the density after light has traversed the sample which has been exposed to radium and D_N is the density obtained when the light has traversed the original sample.³

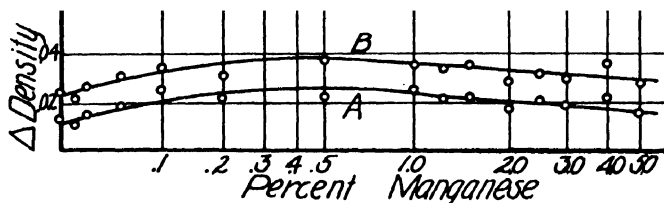


FIG. 9. Absorption change in visible region due to exposure to radium. Curve A, density change in violet portion of spectrum; curve B, density change in red region of spectrum.

The results obtained in this way are presented in figure 9. The values of the manganese concentration are again plotted on a non-uniform scale to spread the values for the lower concentrations. Curve A shows the change in density before and after exposure to radium for the violet portion of the spectrum. To isolate this region Corning Glass Code 554 and Glass Code 306 filters were used in combination. Curve B gives the change in density when the light transmitted was red of wave lengths greater than 6100 Å. The red region was isolated with the aid of a Corning Glass Code 224 filter. It is observed that the change in density in the red region is greater than that in the violet portion of the spectrum. It would appear from these curves that the blue-violet tint which results from the exposure to radium of zinc borate glasses which contain man-

³ The value of the visible absorption is given in terms of the density, because the ultraviolet absorption was expressed in somewhat similar terms. The two are related in that if the density differences are taken as indicated the values of the changes in density on the photographic plate when divided by gamma are comparable with the density obtained by the direct method (see note 2).

ganese is to be attributed to a greater relative change of the absorption in the red region of the spectrum. More important, these curves show that the maximum absorption in the visible region is in the vicinity of 0.5 per cent manganese. As the thermoluminescence optimum is at 0.05 per cent manganese concentration, it appears that there is no direct relationship between the visible color and the thermoluminescence emission.

Curves similar in form to those of figure 9 were obtained when the glasses had been subjected to heat treatment. The results show that the visible color is greatly reduced by prolonged heat treatment, but that any residual color which remains has a maximum in the region of 0.5 per cent manganese and therefore the change in color intensity bears no direct relation to the emission of thermoluminescence. It was also found that both the ultraviolet transparency and the visible transparency of the glasses were restored to approximately their initial values by prolonged heat treatment at 300°C.

SUMMARY

1. The luminescence produced by the exposure to radium of zinc borate glasses which contain manganese indicates that the ordinary rules which govern activators are applicable when radium is the source of the excitation.

2. The optimum concentration of manganese in zinc borate glasses when the luminescence is excited by exposure to radium is 0.05 per cent of manganese.

3. Exposure to radium of zinc borate glasses which contain manganese produces a change in visible color which reaches a maximum at approximately 0.5 per cent of manganese.

4. The violet tint developed by exposure to radium of zinc borate glasses which contain manganese is caused by a greater relative absorption in the long wave-length region of the visible portion of the spectrum.

5. Exposure to radium of zinc borate glasses which contain manganese results in a general increase of absorption in the ultraviolet portion of the spectrum.

6. For each wave length in the ultraviolet region there is a curve which represents the change of absorption as a function of the manganese concentration, and each of these curves has a maximum.

7. The maxima of absorption in the ultraviolet region occur at the same concentrations as luminescence optima.

8. From the results it is inferred that the absorption in the ultraviolet region is closely related to the luminescence which is emitted when the specimens are heated.

9. The initial visible and ultraviolet transparencies are almost completely restored by heating for prolonged periods at temperatures at or above 300°C.

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NEW BOOKS

Practical Methods in Biochemistry. By FREDERICK C. KOCH. Second edition. 23 x 15 cm.: 302 pp. Baltimore: William Wood and Company, 1937. Price: \$2.25.

A manual designed primarily for use by medical students, this book contains an abundance of information and experiments which will be found valuable in biochemistry laboratory courses in general. Sufficient fundamental information is given with each experiment to orient the student properly as to the purpose and meaning of the experiment. References given facilitate the student's interpretation of results obtained.

Two hundred and thirty-two experiments are described. Duplication of methods has been reduced to a minimum in this second edition, those being retained which have been proven to give best results. The preparation of all materials used in these experiments is fully described in an appendix.

There are three parts to the manual. Part I deals with the chemistry of the cell constituents, i.e., carbohydrates, lipids, proteins, and nucleic acids, and with the determination of hydrogen-ion concentration. Part II studies the chemistry of salivary, gastric, and intestinal digestion, and of the bile. Part III contains experiments on blood and hemoglobin, and the quantitative analysis of blood and of urine, with a chapter on the chemical examination of urine for pathological conditions.

DAVID R. BRIGGS.

Principles of Powder Metallurgy. By W. D. JONES. 189 pp. New York: Longmans, Green and Co., London: Edward Arnold and Co., 1937. Price: \$5.00.

This book appears to be the first one written on the subject of powder metallurgy. The author has accomplished his task remarkably well. A large number of references are included and due credit has been given the many research workers in powdered metals. The contents appears to be quite complete and well arranged into six main chapters. About thirty good illustrations are given.

The author begins his treatise by elaborating on the meaning of welding and sintering and shows the influence of many factors, such as particle size and shape, temperature, gases and vapors, and pressure, and methods of application of pressure on sinters.

Shrinkage of sinters, as affected by hot and cold pressing methods, and the physical properties of the resulting sinters are discussed from the standpoint of physics at boundary interface, recrystallization, grain growth, and electrical conductivity. The author also covers compacts of one, two, and three constituents and shows industrial applications and technic in considerable detail in the case of powders of iron, nickel, nickel-iron, chromium, bronzes, tungsten, hard metal carbides such as tungsten carbide, tantalum carbide, diamond-impregnated grinding wheels, etc.

About twenty pages are given to the properties and manufacture of metal powders of carbonyl, electrolytic, pulverized, ground and stamped, and miscellaneous types.

This treatise is exceptionally good and is highly recommended to those interested in powder metallurgy. Throughout the book the author discusses the many factors in an unbiased manner. It is likely that his work will materially aid others in expanding one of the most important fields of metallurgy to many new applications.

RALPH L. DOWDELL.

Polymerization and its Application in the Fields of Rubber, Synthetic Resins and Petroleum. By ROBERT E. BURK (Professor of Chemistry, Western Reserve University), HOWARD E. THOMPSON (Research Chemist, The Harshaw Company), A. J. WERTH (Associate Director of Research of the Bakelite Corporation), and IRA WILLIAMS (Research Chemist, E. I. du Pont de Nemours and Company). Monograph Series No. 75. 15.5 x 23.5 cm.; 312 pp.; 6 fig. New York City: Reinhold Publishing Corporation, 1937. Price: \$7.50.

The object of the authors, as stated in Chapter I, is "to collect facts and theories relative to the subject of polymerization, and to arrange them in a way which will be interesting and helpful to workers in the field." In the first part of the book the theoretical aspect of the subject is presented in five chapters. The latter part of the book is concerned with the industrial applications.

The second chapter, by H. E. Thompson, deals with the relation between molecular structure and the rate of polymerization. The influence of unsaturation, conjugation, substitution of alkyls and halogens, and cyclic structures are reviewed. A quite complete alphabetical list of polymerization catalysts, together with the literature or patent reference, substances polymerized, conditions and products, is found in Chapter III (written by R. E. Burk).

The open-chain mechanism of polymerization as proposed by Carothers, Staudinger, and Solomon is taken up in Chapter IV (by R. E. Burk). A detailed discussion of the mechanism of the polymerization of specific unsaturated and cyclic hydrocarbons and some of their derivatives is included. In the chapter on "The Liquid State and the Structure of Polymers," equations by Staudinger, Raman, Ornstein Andrade, Einstein, and others, giving the relationship between the viscosity of a liquid and some of its physical constants, are discussed.

"Polymerization in the Rubber Industry"—including the field of the synthetic rubbers—is the subject of Chapter VI, written by I. Williams. The seventh chapter, "Polymerization and Synthetic Resins," written by A. J. Werth, includes discussions of the thermoplastic styrene, vinyl, cumar, indene, and petroleum hydrocarbon resins and the thermosetting glyptal, phenol-aldehyde, urea-formaldehyde resins or condensation products, and the relation of their chemical structure to their physical properties.

The final chapter, "Polymerization in the Petroleum Industry," takes up the influence of acids, clay, and other catalysts in the refining processes. This discussion is followed by one on the deterioration of petroleum products, owing to the oxidation and polymerization of the unsaturates, and the rise of inhibitors to prevent oxidation and polymerization. The usefulness and importance of polymerization in the synthesis of asphalt, motor fuels, and lubricating oils are also pointed out.

The numerous references to the literature make the book particularly valuable. The industrial concerns are to be congratulated on permitting publication of the information accumulated by their staffs, and the authors for the very interesting and readable presentation of the subject.

G. B. HEISIG.

THE INFLUENCE OF NEUTRAL SALTS UPON THE INVERSION OF SUCROSE

J. N. PEARCE AND MARGARET E. THOMAS

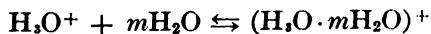
Laboratory of Physical Chemistry, State University of Iowa, Iowa City, Iowa

Received December 20, 1937

The influence of neutral salts upon reaction velocities in general and upon the rate of inversion of sucrose by acids in particular has been the object of a number of researches. Many theories have been advanced to explain the salt effect, and several ideas have been put forth to explain the mechanism of the inversion process.

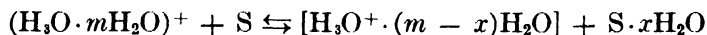
According to the newer theories (2, 5) the salt effect is due to the influence of these interionic forces upon the activities of the reactants and particularly upon that of the oxonium ion. While these theoretical relations apply beautifully to very dilute solutions, they do not always apply so well with solutions of higher salt concentration. According to Hückel the neutral salt effect must always be positive if the substrate has a weaker dipole nature than the solvent. Water has a very strong dipole character.

Over against this theory of interionic force effect and its influence upon reaction velocity is the theory of dehydration dating from Lowenthal and Lenssen (15). According to this theory, the apparent increase in the oxonium-ion activity is due to a removal of water by the hydration of the ions of the added salt. Although a strong advocate of the theory of interionic attraction, Bjerrum (3) states that it is not possible to prove with certainty, for a given ion concentration, what the activity of the ions would be if no forces existed between them. This difficulty is especially noticeable in concentrated solutions. He states also that we must consider the water content of the ions in the solution, for, if the ions form hydrates, the mole fractions, and hence the activities of the ions and of the reactants, will be greater than they would without this hydration. Bjerrum considers only the equilibrium between the oxonium ion and the water, thus



where m is the hydration number. The activity of the water is diminished by the neutral salt effect. According to Bjerrum, the pure neutral salt effect is given by the expression, $(p_0/p)^m$, where p_0 is the vapor pressure of pure water and p is that of the solution. The hydration number, m , has been calculated by various authors and has been found to vary between 8 and 11.

Schmid and Olsen (18) appear to favor the view that dehydration is the principal effect exerted by the neutral salts. Employing the concept of the oxonium ion, the effect is best illustrated by the equilibrium,



Here S refers to the neutral salt, including the ions. Thus the addition of a neutral salt increases the measurable concentration of the oxonium ion.

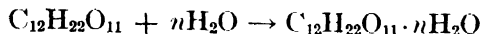
Somewhat earlier Harned (11) found that the effect of the different salts on reaction velocity constants is proportional to their ionic hydration values. He assumes that the increase in the hydrogen-ion activity of hydrochloric acid solutions by neutral salts is due (1) to the high hydration of the hydrogen ion and (2) to the hydration of the ions of the added salt. Scatchard (17) states that the addition of neutral salts will affect the activity of each component. The activity of the hydrogen ion will be increased because of the decrease in the number of water molecules. With decrease in the activity of the water there should be also an increase in the activity of the sucrose. Experiments by Corran and Lewis (4) with cells containing both sucrose and hydrochloric acid showed that both the hydrogen-ion activity and the geometric mean activity are increased by the presence of the sucrose. This should be expected from the relatively high degree of hydration of the sucrose molecule.

MECHANISM OF THE INVERSION PROCESS

The fact that the inversion reaction has not appeared to obey rigidly the law either of a monomolecular or of a bimolecular reaction has led to much discussion. Jones and Lewis (12) believe that the reaction proceeds in two steps. The first consists of a rapid union between a molecule of sucrose and a hydrogen ion, both unhydrated. This complex sucrose-hydrogen ion then reacts with one molecule of water with measurable velocity. Thus they consider the inversion reaction to be typically bimolecular. Fales and Morrell (7) find that the reaction is bimolecular, when the hydrogen-ion concentration lies between 0.01 and 0.03 molar. For higher concentrations, however, the reaction becomes monomolecular, but only after the reaction has proceeded for some time. Euler and Olander (6) agree that the reaction should be regarded as bimolecular, with water acting as one of the reactants. Pennycuik (16) has found that, although the first-order velocity constants apparently increase with time, the deviation from constancy involved when the reaction is considered as monomolecular is not larger than the experimental error. Hence he considers that the velocity constants calculated on the monomolecular basis are acceptable.

It is now quite generally believed that the inversion reaction involves the formation of an unstable intermediate complex and its subsequent

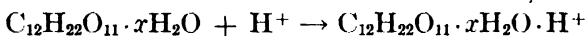
decomposition. The first step is assumed to be the hydration of the sucrose molecule:



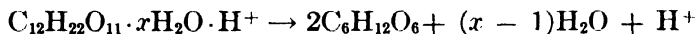
The number of molecules of water of hydration, n , is not definitely known. Fraser and Myrick (8) have found that the degree of hydration of sucrose varies with its concentration. They also found that for a 1 molar solution the osmotic pressure, calculated on the assumption of six molecules of hydrate water, is practically identical with the experimental value of the osmotic pressure at room temperature.

In attempting to determine the number of molecules of water of hydration, Scatchard (17) has resorted to considerations of the probable kinetics and equilibria involved. He found that the monomolecular constant, K , at 20°C. is constant if the sucrose molecule is considered as attached to six molecules of water. The value of K decreases with rising concentration of sucrose when n is less than 6, and increases when n exceeds 6. Although the degree of hydration decreases with rising temperature, the best constancy for K at 40°C. was obtained by assuming n to be 6. Scatchard, therefore, concludes that the hydration of the sucrose molecule must be the first step.

According to Hantzsch and Weissberger (10), the proton attaches itself to the hydrated sucrose molecule to form an intermediate complex, possibly in the form of an oxonium compound. This complex is unstable and decomposes to give the final products of the reaction, glucose and fructose, thus:



which is followed immediately by the reaction,



He considers that the electrical charge on the intermediate complex is the sum of the charges on the reacting molecular species; the charge on the sucrose complex would therefore be positive. The effect of the neutral salts added is determined by the charge on the complex. He states that when the ions in the solution bear the same charge as the complex the effect upon the rate of formation of the complex is positive. Ions having an opposite charge retard the rate of formation of the complex.

Schmid and Olsen (18) find that for those cases in which neutral salts accelerate the reaction velocity, the influence of the salt concentration upon the velocity coefficients may be represented by *

$$K = K_0 \cdot 10^{rM}$$

where M is the molarity of the salt, r is a constant for the specific salt used, and K and K_0 are the velocity coefficients in the presence of the salt

and in the salt-free acid solution, respectively. It has been found that this equation applies for salt concentrations above 0.05 *M*; at lower concentrations the salt effect is linear. Kapanna and Shirkhande (13) have found that the salt effect is given by $K = K_0 e^{aC}$, where *a* is a constant characteristic of the salt and *C* is the molar concentration.

In so far as we have been able to find, practically every study of the rate of inversion of sucrose by acids, whether in the presence or absence of added salts, has involved the use of solutions in which all of the components present are expressed in moles per liter of solution. It is quite evident that an increase in the molar concentration of one constituent must decrease the concentration and hence the activity of the remaining constituents. Since the reaction appears to be monomolecular, it appears logical that the influence of added salts on the inversion velocity can be determined best only when the concentration of the salt is the only variable.

In this paper we present the results obtained from a study of the rate of inversion of sucrose in which all of the components are present in molar proportions. Each solution used contained exactly 0.1 mole of sucrose, 1.0 mole of hydrochloric acid, and *m* moles of salt in 1000 g. of water. The concentration of the salt is the only variable. In this way we hoped to gain further insight into the nature of the neutral salt effect.

MATERIALS AND APPARATUS

The purification of the salts and the preparation of the solutions were performed according to the most approved methods. Conductivity water was used throughout.

The rate of inversion was measured by means of a Schmidt and Haensch triple-field polariscope with a scale readable by two verniers to 0.01°. The 400-mm. inversion tube was surrounded by a nickel jacket which was further insulated by a thick roll of asbestos. Water was forced through the jacket through insulated glass tubes by means of a high-speed Ford water pump connected with a large constant-temperature water bath. The temperature of the bath, as well as that of the inversion tube, was electrically maintained and electrically controlled to within +0.01°C. of the desired temperature. The temperatures of the bath and of the reaction tube were read from two standard thermometers. The intense light from an "Akatos" sodium arc lamp served as the source of illumination.

EXPERIMENTAL PROCEDURE

The required weight of constant-boiling hydrochloric acid solution was placed in a tared glass-stoppered flask. The sucrose and salt were placed in a second similar flask and dissolved in that weight of water which, added to the water of the acid solution, would equal 100 g. The two solutions

TABLE 1

Velocity coefficients for the inversion of sucrose in 1 molar hydrochloric acid solutions with added neutral salts at 25°C.

		F_2	k (MEAN)
Potassium chloride			
0.0000	0.01149	0.01148	0.01149
0.0500	0.01165	0.01165	0.01165
0.1000	0.01189	0.01187	0.01188
0.2000	0.01218	0.01220	0.01219
0.3000	0.01273	0.01262	0.01267
0.5000	0.01338	0.01335	0.01336
1.0000	0.01526	0.01527	0.01527
Sodium chloride			
0.0000	0.01149	0.01148	0.01149
0.0500	0.01174	0.01178	0.01176
0.1000	0.01197	0.01200	0.01199
0.2000	0.01233	0.01235	0.01234
0.3000	0.01287	0.01289	0.01288
0.5000	0.01375	0.01374	0.01375
1.0000	0.01601	0.01599	0.01600
Barium chloride			
0.0000	0.01149	0.01148	0.01149
0.0671	0.01202	0.01205	0.01203
0.1114	0.01228	0.01230	0.01229
0.2003	0.01291	0.01295	0.01293
0.3289	0.01398	0.01397	0.01398
0.4985	0.01501		
0.5046		0.01524	
m	k	m	k
Lithium chloride			
0.2234	0.01239	0.6669	0.01480
0.2236	0.01244	0.6605	0.01490
0.3352	0.01292	0.8013	0.01585
0.3352	0.01295	0.8024	0.01584
0.4481	0.01364	1.0779	0.01781
0.4462	0.01353	1.1128	0.01795
Aluminum nitrate			
0.1003	0.01242	0.3230	0.01532
0.1113	0.01254	0.3244	0.01533
0.1713	0.01343	0.4062	0.01661
0.1754	0.01335	0.4065	0.01658
0.2040	0.01366	0.5225	0.01832
0.2300	0.01405	0.5226	0.01836

were allowed to stand for one hour in the constant-temperature bath at the working temperature. The solutions were then quickly mixed and vigorously shaken. The instant of mixing was taken as the zero time. The resulting solution was then placed in the inversion tube and polari-

TABLE 2

Velocity coefficients for the inversion of sucrose in 1 molar hydrochloric acid solutions with added neutral salts at 35°C.

	k_1	k_2	k (MEAN)
Potassium chloride			
0.0000	0.04461	0.04462	0.04462
0.1000	0.04518	0.04526	0.04522
0.2000	0.04622	0.04625	0.04624
0.4000	0.04896	0.04884	0.04890
0.6000	0.05262	0.05265	0.05264
0.8000	0.05551	0.05530	0.05540
1.0000	0.05891	0.05898	0.05895
Sodium chloride			
0.0000	0.04461	0.04462	0.04462
0.1000	0.04605	0.04614	0.04610
0.2000	0.04772	0.04769	0.04770
0.4000	0.05108	0.05063	0.05085
0.6000	0.05383	0.05407	0.05395
0.8000	0.05798	0.05774	0.05786
1.0000	0.06125	0.06127	0.06126
Barium chloride			
0.1087	0.04654	0.4362	0.05651
0.1073	0.04699	0.6537	0.06110
0.2236	0.05014	0.6687	0.06081
0.2168	0.04997	0.8186	0.06546
0.4366	0.05607	0.8552	0.06756
Aluminum nitrate			
0.1125	0.04950	0.4521	0.06458
0.1127	0.05023	0.6783	0.07514
0.2269	0.05357	0.6789	0.07425
0.2253	0.05389	0.8911	0.08918
0.4482	0.06475	0.8784	0.08893

metric readings were taken until the inversion reaction approached completion.

In the work at 25°C. the rotation angles were read at 15-minute intervals for 3.5 to 4 hours. At 35°C. the time intervals were 5 minutes. Because of the accelerating influence of both the temperature and the

neutral salt, the reactions at this temperature were practically complete in one hour.

The velocity coefficients were calculated by the method of Guggenheim (9). A group of six to eight rotation readings, a_1, a_2, \dots, a_n , were taken at times t_1, t_2, \dots, t_n minutes after mixing. After a constant interval following the initial reading a second series of rotations, a_1', a_2', \dots, a_n' , were taken at times t_1', t_2', \dots, t_n' . This constant interval was taken as 2 hours for readings at 25°C. and half an hour for 35°C. At each temperature the time interval is more than twice the half-time of the reaction. The mathe-

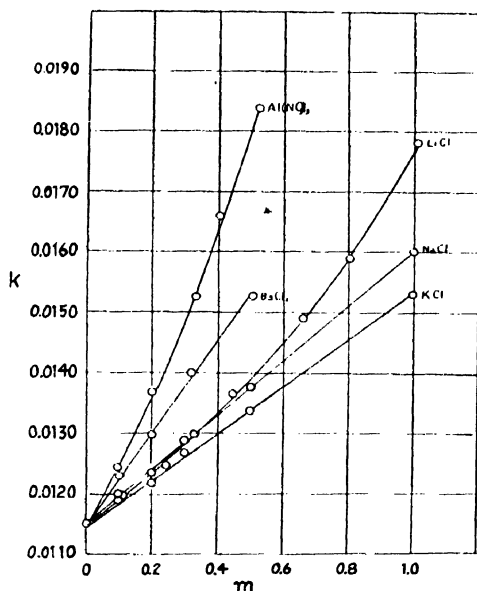


FIG. 1

FIG. 1. Variation of the velocity coefficient with the concentration of the added salt at 25°C.

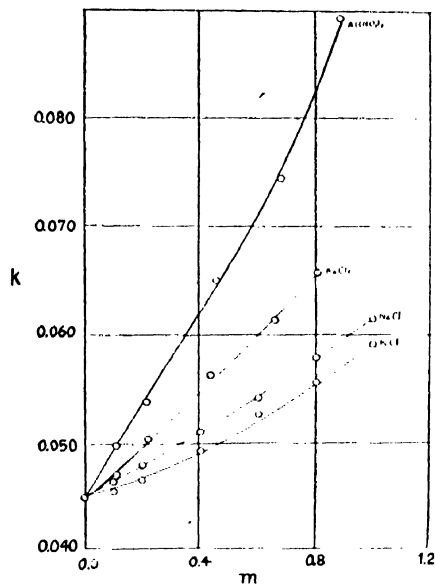


FIG. 2

FIG. 2. Variation of the velocity coefficient with the concentration of the added salt at 35°C.

matical considerations of Guggenheim lead finally to the following equation for calculating the velocity coefficients,

$$2.303 \log \frac{(a_1' - a_1)}{a_2' - a_2} = k(t_2 - t_1)$$

Thus, to obtain the inversion coefficient, k , it is necessary to know only two pairs of readings whose members are $(t_2 - t_1)$ minutes apart. This method has the advantage over others in that it eliminates the use of the uncertain initial and final readings, namely, a_0 and a_∞ .

The final velocity coefficients are recorded in tables 1 and 2. Each value given is the mean of the individual coefficients calculated from at

least two independent series. Here m is molality of the added salt, and k_1 and k_2 are the monomolecular velocity coefficients for two series of the same concentrations. For any given salt concentration the values of k in duplicate series rarely differed by as much as 0.1 per cent at 25°C. and 1.0 per cent at 35°C. It is very evident that the inversion of sucrose

TABLE 3
Temperature coefficients and heats of activation

m	k_{25°	k_{35°	$k_{25^\circ}/k_{35^\circ}$	Q
Potassium chloride solutions				
				<i>calories</i>
0.0000	0.04462	0.01149	3.883	24778
0.1000	0.04522	0.01188	3.806	24429
0.2000	0.04624	0.01219	3.793	24349
0.4000	0.04890	0.01301	3.758	24182
0.6000	0.05264	0.01374	3.831	24530
0.8000	0.05540	0.01451	3.818	24468
1.0000	0.05895	0.01527	3.861	24670
Sodium chloride solutions				
0.0000	0.04462	0.01149	3.883	24778
0.1000	0.04610	0.01199	3.845	24598
0.2000	0.04770	0.01234	3.865	24693
0.4000	0.05085	0.01332	3.818	24468
0.6000	0.05320	0.01420	3.746	24122
0.8000	0.05786	0.01510	3.832	24534
1.0000	0.06126	0.01600	3.829	24519
Barium chloride solutions				
0.0000	0.04462	0.01149	3.883	24778
0.1000	0.04710	0.01230	3.829	24522
0.2000	0.04960	0.01300	3.815	24455
0.4000	0.05460	0.01450	3.760	24215
0.5000	0.05730	0.01540	3.721	23997
Aluminum nitrate solutions				
0.0000	0.04462	0.01149	3.883	24778
0.1000	0.04885	0.01257	3.886	24791
0.2000	0.05310	0.01366	3.886	24791
0.4000	0.06175	0.01627	3.810	24427
0.5000	0.06642	0.01792	3.709	23937

by acids in the presence of added salts is a monomolecular reaction. The variation of the velocity coefficients with the concentration of the added salt at 25°C. is shown in figure 1; that at 35°C. in figure 2.

Recalling that the masses of sucrose, acid, and water have been maintained constant and that only the concentration of the salt has been

varied, we see at once the relative influence of the individual salts. In general, the salt effect increases with increase in the valence of the cation. At 25°C. the inversion rate increases practically rectilinearly with increase in the concentration of the sodium and potassium chlorides. For solutions containing lithium chloride, barium chloride, and aluminum nitrate at 25°C., and for all of the salts at 35°C., the velocity coefficients increase at a continuously increasing rate with increase in the salt concentration. The order of influence of the univalent cations at both temperatures is $\text{Li}^+ > \text{Na}^+ > \text{K}^+$.

The heats of activation, Q , were calculated from the temperature coefficients thus obtained by means of the relation,

$$\log \frac{k_{35}}{k_{25}} = \frac{Q}{4.5787} \left(\frac{T_2 - T_1}{T_2 \cdot T_1} \right)$$

The heats of activation in the salt solutions are slightly lower than in the salt-free acid solutions. The temperature coefficients and the heats of activation are collected in table 3. Both appear to be practically constant and independent of the nature of the salt or its concentration.

DISCUSSION

Followers of Debye and Hückel and of Brönsted would ascribe the influence of the salts upon the inversion velocity chiefly to the increase in the activity of the oxonium ion owing to interionic forces. While the activity of the oxonium ion, and hence the velocity of inversion, may unquestionably be increased in part by the influence of these interionic forces, the relative salt effects of the individual salts are in exact accord with the effects which may be predicted on the basis of ionic hydration. That these cations are hydrated appears to have been definitely established by Webb (19). Working in conjunction with Debye, he calculated the free energy of hydration of the ions as a function of the ionic radii. He found that the free energy of hydration of the ions is not only large, but that it increases rapidly with decrease in the value of the ionic radius, and also with the valence of the ion. With the actual removal of solvent by the hydration of the ions of the added salt the concentration, and, therefore, the activity of the remaining constituents—the sucrose and oxonium ion—must increase; the activity of the water must decrease.

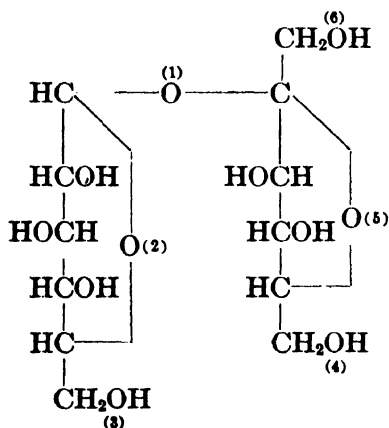
As has been stated, two theories have been advanced as to the rôle played by the solvent in the inversion of the sucrose. According to one, the proton combines with a sucrose molecule and this complex then reacts with a water molecule, giving rise to a bimolecular reaction in which water is one of the reactants. The second assumes the first step to be a hydration of the sucrose molecule, which then combines with a proton to form a $\text{C}_{12}\text{H}_{22}\text{O}_{11} \cdot \text{H}_2\text{O} \cdot \text{H}^+$ complex which decomposes as a first-order

reaction. Since our results show definitely the existence of a monomolecular reaction, the first theory must be excluded. The cryoscopic study of sucrose solutions by Fraser and Myrick (8), as well as the theoretical calculations of Scatchard (17), show definitely that the sucrose molecule becomes hydrated as soon as it is placed in water. For this reason we can hardly say that the first step is one of hydration of the sucrose molecule. It is this hydrated form that is initially present as one of the reactants.

In order to explain the influence of salts upon, and the mechanism of, the inversion process, the structure of sucrose has been studied from the standpoint of modern physics. By means of quantum mechanics Bernal and Fowler (1) have shown that, in addition to its two binding energy centers, the oxygen atom also possesses two non-binding centers. Hence the atom is tetrahedral in form. They postulate for water a structure in which a hydrogen atom of one water molecule is connected to the oxygen atom of an adjacent water molecule through the subsidiary non-binding forces of the oxygen atom. They have shown that the liquid structure of water may be similar to that of quartz, or of cristobalite, or of tridymite, and they further postulate that all three forms are in equilibrium.

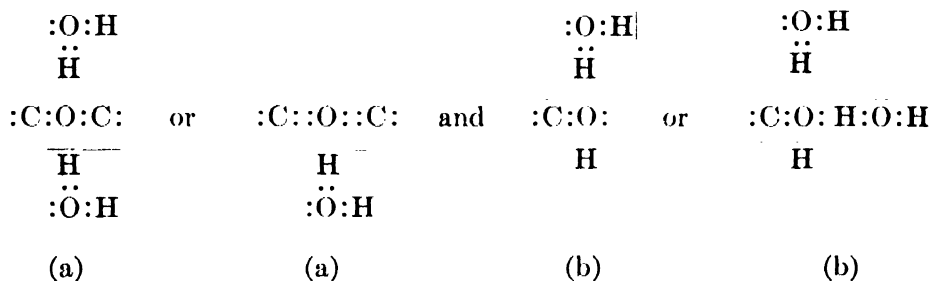
The high solubilities of hydroxide compounds in general, and of sucrose in particular, suggest that the oxygen atoms in sucrose may be connected with water molecules in the same manner. Thus we may be able to think of the sucrose structure as being more or less continuous with that of the water. If this view may be accepted, the maximum number of water molecules which could be attached to one sucrose molecule is eleven, that is, one molecule of water for each oxygen atom in the sucrose molecule. However, since the work of Fraser and Myrick (8) and of Scatchard (17) has shown that the average hydration of the sucrose molecule is six, it is evident that five of these oxygen atoms do not form attachments with water molecules. This may be due to steric hindrance.

While the plane projection of the sucrose molecule, as ordinarily written, is



such a projection does not accurately depict the nature of the molecule. It may be seen that five hydroxyl groups are attached to carbon atoms in the two lactone rings. Because of the stable saturated nature of these rings, the probability of adding water molecules to the oxygen atoms in these hydroxyl groups may be considered as small. Perhaps these, then, are the five oxygen atoms which do not form such attachments. Three oxygen atoms in the sucrose molecule are present in the primary alcohol groups. The well-known hydrating ability of the alcohols suggests that here, at least, continuity of structure with the surrounding water may be said to exist. The remaining three oxygen atoms in the sucrose are present as oxide oxygen. Addition products of oxide oxygen have long been recognized, and therefore it is to be expected that water molecules may also be added at these points. Hence the points at which water molecules are most likely to be added are those at the oxygen atoms, 1 to 6, in the plane projection formula.

Such a connection would be:



where formulas a and b represent the addition of water to the oxide oxygen and to the primary alcohol oxygen, respectively, depending upon whether or not the oxygen is capable of adding one or two molecules of water. If all the oxygen atoms (1 to 6) take on two molecules of water each, the total water of hydration would be twelve molecules. This, however, appears improbable in the light of former work (8, 17). In either case the sucrose is surrounded by a sheath of loosely bound water molecules. Further, it has been shown by Bjerrum and others that the oxonium ion is also physically hydrated to the extent of eight or nine molecules of water.

THE INFLUENCE OF THE ADDED SALT

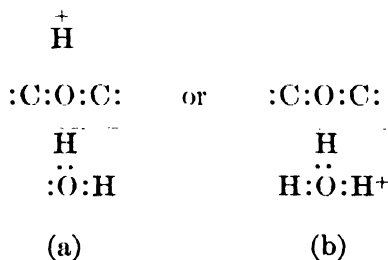
The vulnerable point in the inversion process is at the position of the oxygen atom joining the two branches of the sucrose molecule. It is at this point that the sucrose molecule and the oxonium ion must make intimate contact. Since both are hydrated, the rate of inversion will depend upon the occurrence of favorable collisions between the two,

that is, collisions in which the oxonium ion may approach sufficiently close for a hydrogen atom of the oxonium ion to attach itself to the oxygen atom through coördinate valence linkages. For a given sucrose and acid concentration the probability of such a favorable collision is definite and fixed for a given temperature. Because of decrease of hydration with rise in temperature the probability of favorable collisions, and hence the velocity of inversion, should increase. This is in harmony with experimental data.

The addition of either sucrose or acid alone to water lowers the activity of the water. For this reason the degree of hydration of both should be somewhat diminished and the hydration should be still further reduced by the addition of highly hydrated ions of a dissolved salt. The influence of the salt on the hydration of the uncharged sucrose molecule may be expected to be considerably greater than that on the hydration of the positively charged oxonium ion.

MECHANISM OF THE INVERSION

Is it the proton which combines with a hydrated sucrose molecule, or is it the oxonium ion which combines with the unhydrated sucrose molecule? Thus:



According to Webb (19), for the free energy of hydration of one mole of protons, ΔF is $-249,000$ cals. Unless the protophilic nature of the anhydrous sucrose is comparable with that of water it would appear that it must be the oxonium ion which adds directly to the sucrose oxygen as in formula b. This gives us a hydrated molecular complex containing all of the necessary constituents in the exact proportions for the inversion, and the reaction should be monomolecular. If, on the other hand, the proton adds directly to the oxygen as in formula a, the presence of the positive charge should displace the electronic system of the oxygen in its direction, and thus diminish, if not entirely remove, the possibility of the addition of water. In this case the reaction should be bimolecular, with water as one of the reactants. The rate of reaction would then be dependent upon the probability of favorable collisions between the sucrose-proton ions and the water molecules. For similar reasons the repulsion of

water molecules by the addition of an oxonium ion is also probable, but perhaps to a less extent.

In the light of these considerations we believe that the oxonium ion is added to the unhydrated oxygen of the sucrose molecule, as in formula b, and that the monomolecular reaction which we measure is the decomposition of the resulting complex.

SUMMARY

1. The rate of inversion of sucrose by hydrochloric acid in the presence of neutral salts has been studied at 25°C. and 35°C.
2. It is found that all of the salts used increase the reaction velocity. The order of decreasing effectiveness in so doing is aluminum nitrate, barium chloride, lithium chloride, sodium chloride, potassium chloride.
3. Heats of activation and temperature coefficients were found to be practically constant and independent of the nature of the salt.
4. The effect of salts is explained by the theory of hydration.
5. The hydration of sucrose is attributed to addition of water to tetrahedral oxygen atoms. Hence the structure is believed to be continuous with the liquid water structure proposed by Bernal and Fowler.
6. The accelerating effect of the salts is attributed to decreasing the thickness of the envelope of solvent molecules surrounding the reactants.
7. The mechanism of the reaction is explained to be the addition of the oxonium ion to the sucrose molecule to form a complex, whose rate of decomposition determines the rate of inversion of the sucrose.

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THE INTERFACIAL TENSIONS OF SOME MERCURY-HYDRO-CARBON OIL SYSTEMS. II

J. L. CULBERTSON AND KARL D. LUEDTKE

Laboratory of Physical Chemistry, State College of Washington, Pullman, Washington

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In a recent paper from this laboratory (2) a report was made of a study of the interfacial tensions at mercury-hydrocarbon oil interfaces. Measurements were made in that work by means of the drop-weight method of surface tension determination. In the course of the work it was found impossible to extend the period of drop formation beyond a three-minute interval, else the oil would creep into the tip from which the mercury was dropped, thus vitiating the result. In view of the fact that with certain oils a decrease in the interfacial tension was observed to take place as the period of contact of mercury with oil was increased in length, it was recognized that the approximately three-minute limitation on the period of drop formation rendered it unlikely that the measurements so obtained represented true equilibrium values. It was therefore decided that an effort should be made to determine the extent to which this factor was operative in that work. The capillary-tube method of Bartell and Miller (1) seemed most likely to yield satisfactory results for this system, and hence was chosen for the work. Three objectives were set up: first, to test an apparatus of the type used by Bartell and Miller for interfacial tension measurements involving mercury as one phase; second, to determine whether the measurements previously made by the drop-weight method deviated appreciably from equilibrium values; and third, to observe the effect of some solutes in the oil on the mercury-oil interfacial tension.

APPARATUS AND MATERIALS

The apparatus used in the work was similar to that described and illustrated by Bartell and Miller (1). Owing to the great difference between the densities of the two liquids the cup for the oil was made longer than that for the mercury, since in many cases the height of the oil above the interfacial meniscus was ten times as great as the height of the mercury. Capillary heights were measured on the mercury column by means of a measuring microscope and on the oil column with a cathetometer. The

readings in each case had a precision of ± 0.2 of 1 per cent of the total reading.

The mercury was washed with dilute nitric acid and with water, then dried in air and distilled twice.

Three of the oils which had been used in the previous work (2) were used in order to make a comparison of the methods. A fourth oil was prepared from a water-white paraffin oil (Central Scientific Co.). The preparation consisted in washing, in turn, with several portions of furfural, water, sulfuric acid, water, sodium hydroxide, and finally again with water. The treatment with sulfuric acid portions was continued until no discoloration of the acid was noted even after several hours of agitation with the oil by means of a motor-driven stirrer. After the final washing with water, the oil was dried with calcium chloride, filtered, dried over sodium, refiltered, and then stored over sodium until used. The final product had a molecular weight of 486, as determined by the freezing-point method in benzene, showed no saponifiable matter, and absorbed only a trace of iodine.

RESULTS AND DISCUSSION

The mercury-oil interfacial tension values obtained for the three oils previously used are given in tables 1, 2, and 3 for the temperature range 25°C. to 90°C. For purposes of comparison the values obtained in the previous work (2) are included. Values obtained for the paraffin oil prepared for this investigation are given in table 4, the oil being designated as oil No. 4. In table 4 also are given the interfacial tension values for four systems involving solutions of ethyl bromide and bromobenzene in oil No. 4. The relations indicated in table 4 are graphically shown in figure 1.

As may be observed in tables 1, 2, and 3, the measurements made by means of the capillary-tube apparatus at 25°C. were found to agree very well with the measurements previously made using the drop-weight method, the values being within a 1 per cent range. This was considered a satisfactory check for a mercury-oil system, but it is noteworthy that in all three cases the capillary-tube method yields values slightly lower than the drop-weight method. Since, as was previously indicated, the measurements by the drop-weight method must be made within a limited time of oil-to-mercury contact and no such limitation was necessary with the capillary-tube method, the writers are of the opinion that there is a slight, though real, difference between the measurements made by the two methods, and that the values obtained by the drop-weight method were in no case equilibrium values, although at 25°C. the error involved is very slight. At higher temperatures and in those cases in which in the previous work it had been observed that the interfacial tension decreased

with increase in the time of oil-to-mercury contact, the measurements fell considerably below the drop-weight measurements. Since no reading

TABLE 1
Interfacial tensions of the system mercury-oil No. 1

TEMPERATURE	INTERFACIAL TENSIONS	
	Capillary-tube method (this investigation)	Drop-weight method (reference 2)
°C.	<i>dynes per cm.</i>	<i>dynes per cm.</i>
25	362	364
50	359	362
75	355	360
90	351	359*

* Values at 90°C. for the drop-weight method in this table and tables 2 and 3 are interpolated from a graphic representation of the data in the reference quoted.

TABLE 2
Interfacial tensions of the system mercury-oil No. 2

TEMPERATURE	INTERFACIAL TENSIONS	
	Capillary-tube method (this investigation)	Drop-weight method (reference 2)
°C.	<i>dynes per cm.</i>	<i>dynes per cm.</i>
25	345	348
50	341	343
75	333	max. 339 min. 335
90	325	max. 333 min. 328

TABLE 3
Interfacial tensions of the system mercury-oil No. 3

TEMPERATURE	INTERFACIAL TENSIONS	
	Capillary-tube method (this investigation)	Drop-weight method (reference 2)
°C.	<i>dynes per cm.</i>	<i>dynes per cm.</i>
25	337	339
50	329	332
75	312	325
90	293	max. 323 min. 317

could be obtained in the capillary-tube measurements in less than about fifteen minutes after mercury and oil had made contact (time for the

system to attain constant temperature) and no changes were observed even when a series of observations was made on a single system through a twenty-four-hour interval, it is believed that these represent stable

TABLE 4
Interfacial tensions of the system mercury-oil No. 4

TEMPERATURE	INTERFACIAL TENSIONS				
	Mercury-oil	Mercury-1 per cent ethyl bromide in oil	Mercury-5 per cent ethyl bromide in oil	Mercury-2 per cent bromobenzene in oil	Mercury-5 per cent bromobenzene in oil
°C.	dynes per cm.	dynes per cm.	dynes per cm.	dynes per cm.	dynes per cm.
25	348	333	313	317	309
50	267	263	253	256	249
75	243				
90	237	229	222	225	219

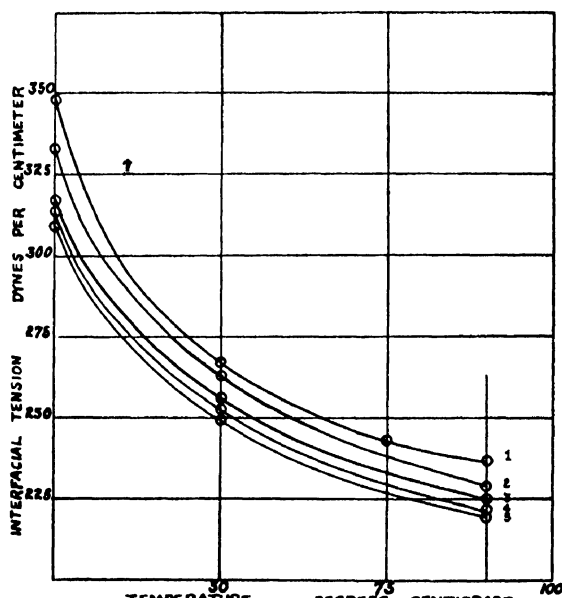


FIG. 1. Interfacial tension values for four systems involving solutions of ethyl bromide and bromobenzene in oil No. 4. Curve 1, mercury-oil No. 4; curve 2, mercury-1 per cent ethyl bromide in oil No. 4; curve 3, mercury-2 per cent bromobenzene in oil No. 4; curve 4, mercury-5 per cent ethyl bromide in oil No. 4; curve 5, mercury-5 per cent bromobenzene in oil No. 4.

values. It would furthermore appear that the results of this investigation are consistent with the idea expressed in the previous paper (2), i.e., that in the case of lubricating oils the evidence indicates progressive adsorption at the oil-mercury interface. This may now be qualified to the extent

that the capillary-tube measurements indicate that the adsorption is substantially complete within a fifteen-minute interval.

The specially prepared oil No. 4 yields an interesting contrast to the others in that the mercury-oil interfacial tension versus temperature curve is decidedly convex toward the axes, while those for Nos. 1, 2, and 3 are slightly concave. The writers are not prepared to offer any adequate theory to account for this difference, though it is no doubt due to differences in surface-active components. The fact that with ethyl bromide and bromobenzene dissolved in the oil (see table 4) the oil mercury interfacial tension is lowered but the shapes of the curves remain approximately the same suggests that in oils 1, 2, and 3 the surface-active components are structurally quite different from the simple brominated compounds.

SUMMARY

The method of Bartell and Miller has been found suitable for interfacial tension measurements at a mercury-oil interface.

Simple brominated hydrocarbons are found to lower the mercury-oil interfacial tension when the bromine compounds are dissolved in the oil.

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ADSORPTION ON CURVED SURFACES AND EMULSIFICATION

HANS M. CASSEL

Colgate-Palmolive-Peet Company, Jersey City, N. J.

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The increase of the vapor pressure (potential) of a one-component liquid, owing to an increase of the curvature of its surface, can be described, from the thermodynamical point of view, as a consequence of the capillary pressure exerted upon the internal phase on account of the surface tension. From the molecular point of view, on the other hand, this effect is to be understood as the reduction of the attractive field, owing to the removal of the fluid masses contained in the interspace between the tangential plane and the spherical body of the liquid. Although the same considerations, undoubtedly, hold in the case of adsorbed molecules bound by a spherical adsorbent, the change of the potential of the adsorbed substance as a function of the curvature of the adsorbing surface, apparently, has not been treated thermodynamically.

The following deductions concerning this problem are based entirely upon the Gibbsian theory of capillarity.

THERMODYNAMIC THEORY

We consider a spherical mass of radius, r , consisting of a solvent (1) and a capillary-active substance (2) dissolved in it being in equilibrium with the vapor (external) phase containing the same two components. By μ_1 , μ_2 we shall designate the potentials; by c_{1in} , c_{2in} and c_{1ex} , c_{2ex} the concentrations (masses per unit volume) of the components in the internal and external phases, respectively. We also have to take into consideration, of course, the interface between the homogeneous phases with the superficial densities Γ_1 and Γ_2 . Let p_{ex} and $p_{in} = p_{ex} + \sigma C$ be the total pressures in the external and internal phases, where σ denotes the interfacial tension and $C = 2/r$ the curvature, supposing that the radius is sufficiently defined by the size of the internal mass.

The problem we have to deal with concerns the potential, μ_2 , of a film of a given density, Γ_2 , as a function of the curvature, C ; i.e., we wish to know the value of the differential coefficient, $\left(\frac{\partial \mu}{\partial c}\right)_{\Gamma_2}$, as a function of the

interfacial tension, the curvature, and the mass distribution given by the c_{1in} , c_{2in} and c_{1ex} , c_{2ex} .

Generally, μ_2 is a function of Γ_2 , μ_1 , and C , so that

$$d\mu_2 = \frac{\partial \mu_2}{\partial \Gamma_2} d\Gamma_2 + \frac{\partial \mu_2}{\partial \mu_1} d\mu_1 + \frac{\partial \mu_2}{\partial C} dC \quad (1)$$

On the other side, for a given curvature, Γ_2 is a function of μ_1 and μ_2 :

$$d\Gamma_2 = \frac{\partial \Gamma_2}{\partial \mu_1} d\mu_1 + \frac{\partial \Gamma_2}{\partial \mu_2} d\mu_2 \quad (2)$$

For $d\Gamma_2 = 0$ we therefore obtain:

$$\left(\frac{d\mu_2}{dC} \right)_{\Gamma_2} = \frac{\partial \mu_2}{\partial \mu_1} \frac{d\mu_1}{dC} + \left(\frac{\partial \mu_2}{\partial C} \right)_{\mu_1} \quad (1a)$$

and

$$\frac{\partial \mu_2}{\partial \mu_1} = - \frac{\partial \Gamma_2}{\partial \mu_1} / \frac{\partial \Gamma_2}{\partial \mu_2} \quad (2a)$$

The establishment of equilibrium, furthermore, requires the following equations (of state) to be fulfilled simultaneously:

$$dp_{in} = C_{1in} d\mu_1 + C_{2in} d\mu_2 \quad (3a)$$

$$dp_{ex} = C_{1ex} d\mu_1 + C_{2ex} d\mu_2 \quad (3b)$$

$$-d\sigma = \Gamma_1 d\mu_1 + \Gamma_2 d\mu_2 \quad (3c)$$

Hence we may derive the relation:

$$\frac{\partial \Gamma_1}{\partial \mu_2} = \frac{\partial \Gamma_2}{\partial \mu_1} \quad (4)$$

as an expression of the "displacement effect" (4).

Consequently equation 1a, because of equation 2a, can be written in the form:

$$\left(\frac{d\mu_2}{dC} \right)_{\Gamma_2} = - \frac{d\mu_1}{dC} \cdot \frac{\partial \Gamma_1}{\partial \mu_2} / \frac{\partial \Gamma_2}{\partial \mu_2} + \left(\frac{\partial \mu_2}{\partial C} \right)_{\mu_1} \quad (5)$$

Now, for the case of plane surfaces, Gibbs (12) has shown that we can consider the dividing surface as being located so that the total quantity of the first component in the vicinity of the surface of discontinuity is the same as if the density of this component were uniform on each side quite up to the dividing surface. Such a location might be objectionable only with regard to a component which has very nearly the same density in the adjacent phases.

Extending this procedure to the case of curved surfaces we could say that the radius of the dividing surface had to be determined so as to make

the quantity Γ_1 vanish. However, an even less restrictive demand is implied in the assumption that the value of Γ_1 shall be constant for a given value of the curvature. On this basis it is justified to consider $\partial\Gamma_1/\partial\mu_2$ as very small in comparison to $\partial\Gamma_2/\partial\mu_2$ and to use

$$\left(\frac{d\mu_2}{dC}\right)_{\Gamma_2} = \left(\frac{\partial\mu_2}{\partial C}\right)_{\mu_1} \quad (6)$$

as a reasonable approximation.

If, finally, we take into account the condition of mechanical equilibrium:

$$dp_{in} - dp_{ex} = \sigma dC + Cd\sigma \quad (7)$$

we obtain the result:

$$\left(\frac{d\mu_2}{dC}\right)_{\Gamma_2} = \frac{\sigma}{c_{2in} + C\Gamma_2 - c_{2ex}} \quad (8)$$

In perfect analogy to the behavior of a one-component droplet (Gibbs-Thomson formula), the potential of a film of given thickness (density), Γ_2 , is larger upon the smaller droplets than upon the larger ones if

$$C_{2in} + C\Gamma > C_{2ex} \quad (9)$$

whereas the opposite will be true if

$$C_{2ex} > C_{2in} + C\Gamma_2 \quad (10)$$

In other words, for a given potential, μ_2 , under the first condition (inequality 9) the films of greater curvature must be thinner; under the second condition (inequality 10), however, they must be thicker than those of smaller curvature. This might be formulated quantitatively:

$$RT \frac{\partial \log \Gamma_2}{\partial C} = \frac{-\sigma}{c_{2in} + C\Gamma_2 - c_{2ex}} \quad (11)$$

In regard to the analogy with droplets in bulk the inequality 10 will be considered as the "stability criterion" for films of given curvature and interfacial density.

Some consequences drawn from this definition will be briefly discussed.

The decision as to whether or not condition 10 can be satisfied depends entirely on the individual shape of the adsorption isotherm represented in a Γ_2 - c_{2ex} diagram (see figure 1). Here it is assumed as a first approximation that the course of the isotherms does not vary with the curvature. The adsorption isotherms A and A' correspond to those of the normal type, the latter representing an increase of the adsorption as possibly due to a lowering of the temperature. On the other hand, the stability condition is represented in the Γ_2 - c_{2ex} diagram by the course of the discriminant line:

$$\Gamma_2 = r/2 (c_{2ex} - c_{2in}) \quad (12)$$

only those parts of the isotherms located below the discriminant corresponding to "stable states" of films with given curvature. Since the discriminants are approximately straight lines starting in the origin of the diagram, there may occur one or two intersections with the isotherms or none at all.

If we had to deal with monolayers only, the isotherms would reach saturation and only one intersection of the discriminants could occur, but we know, principally from the work of Perrin (16), that, for instance on the surface of soap solutions, a multiplicity of layers can exist. This means that the isotherms surpass saturation, as could also be shown in the case of other organic molecules adsorbed from the vapor phase on mercury (7, 8). Then, of course, a second intersection may take place.

In general, a minimum concentration, c_{2ex} , has to be reached before stability is possible, and, in case of the second intersection, a definite maximum concentration cannot be surpassed without annihilating the stability

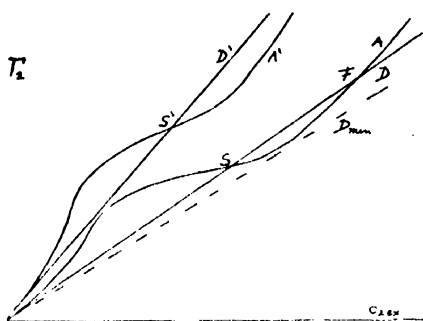


FIG. 1

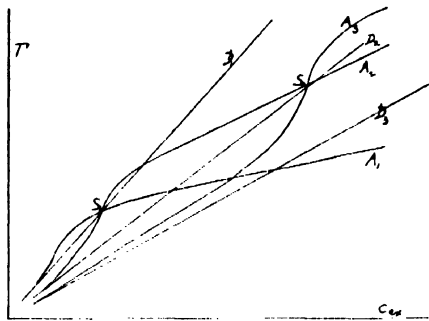


FIG. 2

Moreover, for any given isotherm, a minimum radius must be guaranteed in order to obtain stability (see the tangent discriminants in figure 1).

If the course of the isotherm is shifted in the direction of smaller concentrations (as indicated by the isotherm A'), the range of stability on a given discriminant, i.e., for a given curvature, shrinks more and more until the isotherm fails to be cut. Stability, then, is possible only for discriminants of a steeper slope, i.e., for films of larger radii.

It might, finally, be emphasized that the present deductions are not restricted by the special assumptions concerning the adsorption isotherms as drawn in figure 1.

On the basis of equation 11 the influence of the curvature upon the course of the isotherms may be easily derived. In figure 2 the essential features of this effect are shown for a series of adsorption isotherms, A_1 , A_2 , A_3 on surfaces with presumably increasing curvatures $r_1 > r_2 > r_3$. The intersections S_1 , S_2 , S_3 with the discriminants D_1 , D_2 , D_3 are now spread over a wider range instead of defining a sharp limit.

COMPARISON WITH EXPERIMENTAL FACTS

No direct experiments seem to be available which would allow of a verification of this theory. An indirect test, however, is possible in the field of emulsions (5, 6).

By the word "emulsion" we will understand a dispersion of finely divided droplets or gas bubbles suspended in a liquid medium. Tolman (18) has shown that such systems are thermodynamically stable only if the interfacial tension is zero. Otherwise they collapse as time goes on and change to the stable state of two coexisting masses in bulk. However, a "pseudo-stabilization" may be obtained, at least to a certain degree, by the addition of a third component, the emulsifying agent, which is soluble in the external phase and produces a film around the particles, thus preventing their coalescence (9). This implies the assumption that the growth of solvent droplets through condensation is negligible.

One has to be aware, however, that the collision of particles does not necessarily result in their coalescence, i.e., in the formation of larger homogeneous units. In many cases, usually regarded as examples of reversible coagulation (the terms "agglutination" and "flocculation" are applied in different fields), the particle boundaries are preserved, being separated and sticking together by means of the interfacial layers of emulsifying agent.

According to the present aspect the coagulation is simply understood as due to the capillary condensation of the emulsifier in between adjacent particles, which naturally must occur if the stability condition, defined above, is not fulfilled. Generally coagulation has to be considered as the pre-stage of final coalescence.

In comparing the present theory with experimental facts we introduce the somewhat hypothetical assumption that the criterion, $\partial\mu_2/\partial C < 0$, represents a necessary condition for the pseudo-stability of emulsions, but one has to keep in mind that it can *not* be a *sufficient stability condition*. For this condition might well be satisfied also when the films are not thick enough to exert the protective action. Moreover, the compensation of gravity is necessary, which may be partially ascribed to the Brownian movement, and partially to the electric forces of adsorbed ions.

Since the potential of the external solvent present in the case of emulsions is almost independent of the variations in concentration of the other components which always form sufficiently dilute solutions, the formulas derived above are applicable without alterations. (To destroy any doubts one might consider the same assumption to be the basis of the generally acknowledged pH scale!)

THE INVERSION OF EMULSIONS

As a matter of fact, two types of emulsions may be formed with the same solvents (15). The decision as to which phase is to be the dispersing

agent depends greatly on the nature of the emulsifying substance. Alkali soaps, which are readily soluble in water and far less soluble in oil, give oil-in-water emulsions, while soaps of other bases, whose solubility is greater in oil, yield the water-in-oil type (2). Generally the rule of Bancroft holds, that the better solvent for the emulsifier is the external phase. This statement is in full conformity with the stability condition for the films as defined above.

A few exceptions stand in the way of acknowledging the generality of Bancroft's rule (2). For instance, oleic acid is soluble in benzene but not markedly soluble in water. Contrary to expectation, however, benzene is actually emulsified in water. Other examples are those of ethyl ether and some organic solvents emulsified in water, supposedly by the action of iodine as emulsifier.

From the standpoint of the present theory, it seems probable that in these cases a fourth component not taken into consideration has actually operated in producing the protective film. In this regard, the oxygen of the air is open to suspicion because, in the presence of air, unsaturated acids as well as ether easily undergo changes. Undoubtedly, the possibility of emulsification offers a very sensitive analytical test for certain compounds, the type of emulsion obtained, furthermore, allowing a statement concerning their relative solubility.

In the case of supposedly insoluble emulsifiers, as, for instance, soot or alumina, we remain in agreement with the theory by regarding the particles of these substances as the molecules dissolved in the adjacent phases, the solubilities being regulated by the interfacial energies of these "molecules" (14). This view of the mechanism of emulsification is practically identical with that first suggested by Ramsden (17).

THE STABILITY RANGE OF EMULSIONS

The theory provides that an excess as well as the removal of the emulsifier causes the collapse of emulsions. This explains the fact that for the practice of preparing emulsions it is advisable to apply the emulsifier in small portions instead of as a whole.

An obvious confirmation of the theory is the observation of Bartsch (3) and others that optimum concentrations of stabilizing agents exist for the durability of dispersed systems.

Experiment, furthermore, proves the theoretical expectation that the size of the emulsified particles is limited by a minimum radius. For example, Kistler (13), applying a colloid mill for the emulsification of water in toluene with aluminum stearate as the emulsifier, could not detect droplets smaller than 0.2μ in diameter, estimated microscopically.

The theory also explains the otherwise astonishing fact that (9) the stability of emulsions can be noticeably improved by "homogenization",

i.e., by reducing the radii of the droplets and decreasing the concentration of the emulsifying agent through the development of new surfaces.

Finally, the theory accounts for the "salting out of emulsions" without recurring to the simple idea of neutralizing the electric surface charges. The effect of electrolytes upon the emulsifying agents, if it is not a chemical reaction, consists in changing their activity coefficients (10). Accordingly, in case of increased activity (2, 11), the adsorption isotherm must be shifted into the direction of lower concentrations. The effect upon the stability of an emulsion, under such conditions, corresponds to the effect of temperature changes, as described in connection with figure 1.

But reliable data are lacking for decision as to whether or not the breaking of emulsions by heat treatment is in agreement with the theoretical deductions. Probably the thermal effects can be understood only if the conditions sufficient for emulsification are also taken into account.

CONCLUSION

The theory, on the whole, is in satisfactory agreement with the facts known about emulsions. However, experiments are missing which would permit a quantitative test in detail.

On the other hand, it seems to be allowable to extend the theory here developed to the inhibiting action of "protective colloids" and "peptizing agents" in general.

SUMMARY

The thermodynamic theory of adsorption on curved surfaces leads to a relation analogous to the Gibbs-Thomson formula for the vapor pressure of droplets as a function of the curvature. In regard to the lack of direct experiments the theoretical expectations are checked by experience with emulsions. The basic idea is that emulsions can be stable only if the interfacial density of the emulsifying films is greater for surfaces of larger than for those of smaller curvature. There are no data available which would allow a quantitative comparison, but no facts seem to be known which are in contradiction with the theory.

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AN INVESTIGATION OF THE LANTHANUM AMALGAM ELECTRODE FOR PRECISE ELECTROMOTIVE FORCE MEASUREMENTS¹

W. GEORGE PARKS AND RICHARD W. KINGERLEY

Department of Chemistry, Rhode Island State College, Kingston, Rhode Island

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INTRODUCTION

The purpose of this investigation was to determine whether a suitable galvanic cell involving a lanthanum amalgam electrode could be constructed for precise E.M.F. measurements. A need for such measurements arises from the fact that, with the exception of the work of Hakomori (7) on indium chloride, there has been very little data obtained on electrochemical cells involving salts of trivalent metals.

The more common trivalent metal salts, such as those of iron, chromium, aluminum, and indium, are highly hydrolyzed in aqueous solution and do not lend themselves to precise E.M.F. measurements. The addition of an acid to prevent hydrolysis introduces a difficult correction factor when the data are treated theoretically. Attention is turned to lanthanum which, according to Ley (18), is not hydrolyzed to any appreciable degree. If this metal can be developed into a reproducible electrode, it will give free energy measurements that may be employed to test further the interionic attraction theory of Debye and Hückel as extended by LaMer, Gronwall, and Greiff (14) for electrolytes of the unsymmetrical valence type. Furthermore, if the temperature coefficients of the cell are obtained, certain thermodynamic quantities of the cell process can be calculated by means of the Gibbs-Helmholtz equation. The free energy change for the cell process, the entropy, and the heat capacity may also be investigated.

Müller (21) carried out an investigation of certain electrochemical cells with lanthanum. He was interested primarily in the effect of varying the lanthanum content of the amalgam rather than the concentration of the salt. Furthermore, his cells contained a salt bridge, which introduces factors that are difficult to treat theoretically. His data were not reproducible enough to give significant results when subjected to a rigorous mathematical treatment.

¹ This article is based upon a thesis submitted by Richard W. Kinglerley to the Faculty of Rhode Island State College in partial fulfillment of the requirements for the degree of Master of Science in Chemistry, June, 1937.

PREPARATION OF MATERIALS

Lanthanum salts

Several salts of lanthanum were investigated in order to obtain a very pure sample of lanthanum oxide. The most likely impurities in a sample of any lanthanum compound would be the rare earths, principally cerium and praseodymium. Cerium was tested for by the hypochlorite method of Baxter, Tani, and Chapin (4) and found to be absent in all samples. In testing for the presence of the rare earths, absorption spectra of several aqueous salt solutions were taken. Lanthanum is the only one of its group that does not give an absorption in the visible range (25). Any visible absorption was checked against the iron arc for wave length and then identified. A c.p. sample of lanthanum chloride showed absorption bands at 4445 Å., 4654-4667 Å., and 4775-4789 Å. in a 1 *N* solution through 13.5 cm. of solution on an Eastman 40 plate at 2 minutes exposure. This absorption corresponds definitely to that of praseodymium as described by Yntema (25), and indicates approximately 0.5 per cent. A sample of lanthanum ammonium nitrate obtained from the Maywood Chemical Co. showed no absorption and therefore was selected as the starting material.

Lanthanum oxide

Approximately 200 g. of lanthanum ammonium nitrate was dissolved in half a liter of water, and the solution filtered free from any insoluble matter. To this solution was added slowly with stirring a saturated solution of oxalic acid until precipitation was complete. It was then stirred for an hour and filtered on a Büchner funnel with abundant washing to remove soluble salts. This precipitated lanthanum oxalate was then ignited in a platinum dish for 4 hours at a temperature of 600°C. According to Kolthoff and Elmquist (13), the oxalate is completely decomposed at this temperature. The lanthanum oxide was preserved in a glass-stoppered bottle and was used for the preparation of all lanthanum salts.

Lanthanum chloride

Forty grams of the prepared lanthanum oxide was suspended in water and treated with slightly less than the required amount of hydrochloric acid. The lanthanum chloride was then recovered from the filtered solution. Since the salt is exceedingly soluble in water and extremely deliquescent, the ordinary methods of recrystallization were not applicable. It was necessary to pump off the water in a vacuum desiccator and then to remove the water of crystallization by continued pumping for 5 days at 90°C. (22). Analysis showed this salt to have one molecule of water of crystallization instead of seven, as when it crystallizes from water.

Repeated attempts to remove this last molecule of water resulted in decomposition of the salt into a basic chloride (8). This decomposition took place either on prolonged heating at 90°C . or upon shorter heating at any temperature above 100°C . Therefore the $\text{LaCl}_3 \cdot \text{H}_2\text{O}$ was used. It was preserved in a glass-stoppered bottle sealed with paraffin.

Mercury

Redistilled mercury was stirred with dilute nitric acid overnight and then twice distilled by the Hulett (9) method in a slow current of air.

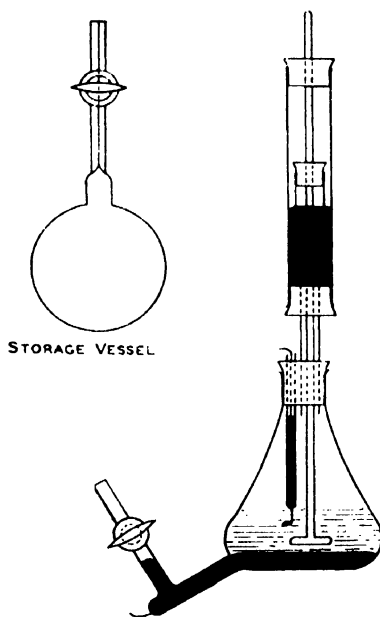


FIG. 1. Apparatus for preparation of amalgams

Lanthanum amalgam

The lanthanum amalgam was prepared by electrolysis of $\text{LaCl}_3 \cdot \text{H}_2\text{O}$ in absolute ethyl alcohol using a mercury cathode (2, 11). The solution was made by dissolving 40 g. of the salt in 100 cc. of alcohol. Any slightly cloudy appearance in the solution was removed by centrifuging it for a short time. The electrolytic cell construction is shown in figure 1. It was made by sealing a right-angled bend with a glass stopcock, as shown, into the bottom of a 250-cc. Erlenmeyer flask. A platinum wire was sealed into the glass bend for electrical connection to the pool of mercury. In this cell was placed the alcoholic solution, together with 600 g. of mercury. The flask was stoppered with a rubber stopper that admitted a platinum anode and an air-tight mercury-sealed stirrer for agitation of the mercury. The whole system was cooled continuously by running

water. A potential of 50 volts was applied, which allowed a current of 0.3 ampere per square centimeter of mercury surface to flow. The water successfully kept the solution cool over a considerable period of time. The current was passed through the solution for 20 hours. Then the cell was tipped and the amalgam drawn through the stopcock into a bulb also shown in figure 1. The bulb was alternately evacuated and filled with nitrogen to remove last traces of oxygen, and then the amalgam set aside until used.

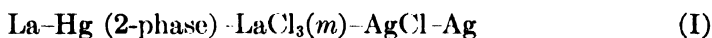
Nitrogen

Tank nitrogen was purified by passing it through potassium pyrogalate, sodium hydroxide, and sulfuric acid. The gas was then passed over heated copper gauze in a quartz tube to remove last traces of oxygen. Finally, before entering the cell vessel it was passed over soda lime and calcium chloride, and then through a saturating column containing a solution of the same concentration as that in the cell.

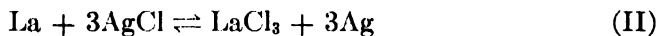
EXPERIMENTAL METHODS

Cell and electrodes

An attempt was made to construct a cell that would successfully measure the electrode process between lanthanum and one of its salts. Lanthanum chloride appears to be the most suitable salt, as it can be prepared readily. The silver-silver chloride reference electrode is standard and very reproducible (5). Therefore it appeared logical to try first to measure the cell



in which the cell reaction is represented by



Lanthanum metal is very reactive and readily combines with oxygen to form the oxide or with water to form the hydroxide. The amalgam is even more active. It is therefore necessary to use some type of cell that will allow the lanthanum amalgam to remain in contact with the solution for only a brief period of time. The dropping electrode used by Lewis and Kraus (16), MacInnes and Parker (19), and Richards and Conant (24) was adapted with some modifications. If the apparatus is successful it will allow measurements to be made before any appreciable reaction takes place between the amalgam and the solution. This dropping electrode is shown by A in figure 2. It consists of a tube of 30-cc. capacity to which are sealed four stopcocks; three of them are sealed in short arms on the top of the electrode and one is sealed in the bottom. The lower stopcock is part of a long capillary tube which is bent in the form of a hook at the bottom. Into this capillary tube and just below the lower stopcock is

sealed a platinum wire with a connecting tube for electrical contact. When this electrode is in use, the bulb can be filled with amalgam and placed in the cell vessel. By turning stopcock 1 a drop of amalgam can be balanced upon the upturned end of the capillary tube, and, as electrical connection is provided for through the amalgam column, the potential developed between this drop and the standard electrode can be measured. The electrode vessel, shown by B in figure 2 and also by C (top view), is composed of a central compartment from which extend three side arms.

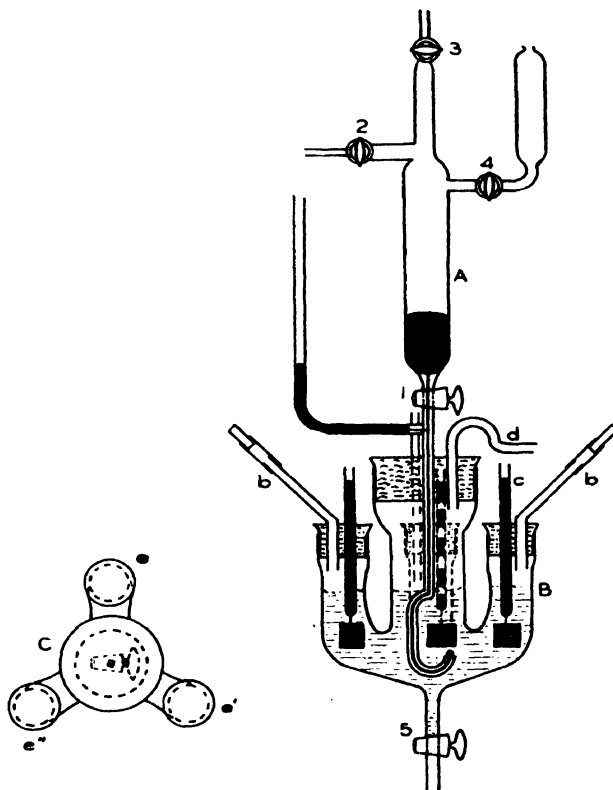


FIG. 2. Electrode vessel

Each of these arms, *e*, *e'*, *e''*, contains a reference electrode and a small glass tube, *b*, bent at 60° for introducing nitrogen into the cell. The tube, *d*, in the top of the cell is the exit for nitrogen gas. Having three reference electrodes serves as a convenient means of checking the constancy of each half-cell. The stopcock 5 at the bottom of the vessel is for removing the amalgam after measurements have been made. This prevents any reaction between the amalgam and the solution due to continued contact. The technique for filling the cell was as follows: A 0.03 molal stock solu-

tion of the lanthanum chloride was made up and diluted by volume to the required concentration for each measurement. After carefully cleaning and drying the electrode vessel, 100 cc. of this lanthanum chloride solution was introduced, and the three silver-silver chloride electrodes and nitrogen tubes put in place. A large stopper was placed in the top of the central compartment, and the cell placed in the constant-temperature oil bath while the dropping electrode was assembled. After being carefully cleaned and dried, the electrode was alternately filled with nitrogen and evacuated to remove oxygen. The amalgam was introduced into the tube by placing the amalgam reservoir in boiling water until it became one phase and then connecting it to the vertical arm of the electrode. Any oxide which formed on the surface of the amalgam was removed by filling the electrode through the fine capillary on the end of the reservoir. A slight pressure of nitrogen was introduced above the amalgam to facilitate its flow through the capillary. The dropping electrode was then put into place in the cell vessel and the whole unit clamped firmly in the oil bath. Nitrogen was now bubbled slowly through each leg of the vessel for 20 minutes. At the end of this time the tubes were sealed by means of a short piece of rubber and a glass plug. The cell was allowed to remain in the bath for 2 hours before any measurements were attempted.

In making measurements stopcock 1 was opened and the amalgam allowed to run down the capillary and form a single drop on the end. The potential was measured as soon as possible and repeated every minute for a period of about twenty minutes. At the end of this time another drop was formed and its potential measured against one of the other reference electrodes. This process was continued for a period of 3 hours and then the cell was discarded. Measurements were taken at eight concentrations and three temperatures. In many cases duplicate determinations were made to check the results.

Preparation and analysis of lanthanum chloride solutions

For all concentrations of lanthanum chloride less than 0.03 molal the solutions were made from the stock solution by dilution. The stock solution was analyzed by the method suggested by Jukkola, Audrieth, and Hopkins (11). The lanthanum was precipitated in a neutral solution as the oxalate and ignited to the oxide. It was possible to obtain triplicate determinations to check within 0.1 per cent. Several cases gave results to agree within 0.03 per cent. Other methods of analysis were tried, including the precipitation of the chloride as silver chloride and the titration of the precipitated lanthanum oxalate with potassium permanganate. These methods were abandoned, as they were not as reproducible as the oxide procedure.

Analysis of the amalgam

In the preparation of the lanthanum amalgam the electrolysis was continued for a sufficient time to produce two phases. The time was calculated from the solubility of lanthanum in mercury as determined by Parks and Campanella (22). As long as a two-phase amalgam existed it was not necessary to know the exact concentration of lanthanum. However, each new supply of amalgam prepared was analyzed. This was accomplished by allowing a sample of amalgam to remain in contact with the air for a period of 10 days. The lanthanum separated from the mercury as a white solid consisting of lanthanum hydroxide and carbonate. According to several investigators (2, 20) this separation is complete. To the precipitate 0.1 *N* hydrochloric acid was added and the liquid was brought to a boil. The solution was back titrated with standard sodium hydroxide and the per cent of lanthanum was calculated.

The apparatus

For maintaining the cell at constant temperature a large oil thermostat with automatic heating and cooling coils was used. The desired temperature was maintained to $\pm 0.05^\circ\text{C}$. The Beckmann thermometer was checked against a laboratory standard certified by the Bureau of Standards. The potentiometer was a Leeds and Northrup type K with a high-resistance galvanometer, external critical damping resistance 2300 ohms, and a period of 3.0 seconds. The potentiometer was calibrated and checked against a certified Weston standard cell.

EXPERIMENTAL DATA

Constant potentiometer readings were not obtained when the drop was formed on the electrode. A constant shift in the E.M.F. was observed, which increased with increasing temperature. After considerable investigation it was found that the maximum E.M.F. developed could be reproduced within 1 millivolt. In table 1 is given an example of the measurements taken.

A maximum E.M.F. was reached after approximately seven minutes at this temperature. However, in some cases the maxima were not reproducible and some showed several inflection points. All readings except the best were discarded. The cause of the drifting E.M.F. is undoubtedly due to the reaction of the amalgam with the solution. In order to determine whether this maximum was of any value it was measured at eight different concentrations of lanthanum chloride at 0° , 25° , and 50°C . Then, using the equation

$$E'_0 = E_0 + \frac{Nu}{n} \frac{RT}{F} \ln m \quad (\text{III})$$

TABLE 1

Variation of the E.M.F. of the cell $\text{La-Hg}(2\text{-phase})\text{-LaCl}_3(m)\text{-AgCl-Ag}$ with time
Temperature, $25^\circ\text{C}.$; $0.0010\text{ }M\text{ LaCl}_3$

TIME IN MINUTES	DROP NO. 2	DROP NO. 4
1	1.5139	1.5133
2	1.5311	1.5188
3	1.5341	1.5199
4	1.5368	1.5251
5	1.5454	1.5390
6	1.5572*	1.5548
7	1.5560	1.5556
8	1.5535	1.5559*
9	1.5540	1.5529
10	1.5500	1.5489
11	1.5524	1.5452
12	1.5516	1.5439
13	1.5483	1.5422
14	1.5462	1.5410
15	1.5439	1.5400

* Maximum.

TABLE 2

Maximum electromotive force of the cell $\text{La-Hg}(2\text{-phase})\text{-LaCl}_3(m)\text{-AgCl-Ag}$

Lanthanum amalgam.....	$0^\circ\text{C}.$		$25^\circ\text{C}.$		$50^\circ\text{C}.$	
	0.055 per cent		0.018 per cent		0.025 per cent	
MOLALITY	$E_{\text{obs.}}$	E'_0	$E_{\text{obs.}}$	E'_0	$E_{\text{obs.}}$	E'_0
0.02162	1.154	1.034	1.191	1.060		
0.01082	1.201	1.059	1.335	1.180		
0.006187	1.220	1.060	1.407	1.233		
0.004922	1.235	1.068	1.433	1.251		
0.003610	1.271	1.094	1.461	1.268		
0.001970	1.313	1.118	1.521	1.308		
0.001032	1.367	1.151	1.558	1.324		
0.005280	1.454	1.217	1.586	1.327		
0.02247					1.290	1.149
0.01125					1.383	1.216
0.006428					1.461	1.374
0.005115					1.502	1.306
0.003753					1.536	1.329
0.002048					1.628	1.397
0.001075					1.678	1.423
0.0005495					1.716	1.437

values for E'_0 were calculated and plotted against the square root of the concentration. The results are shown in table 2 and figure 3. The curves shown in figure 3 should be parallel, since the difference at any given con-

centration should be governed entirely by the temperature coefficient of the E.M.F. However, the curves are not only not parallel, but at 0°C. the curve approaches the potential axis at a very high value, if not infinity. It follows from this that the cell process (II) must be complicated by a side reaction. After careful investigation it was found that in addition to the true cell potential, the hydrogen overvoltage was being measured. This conclusion was reached from the fact that a drop of amalgam on standing a short time in contact with some of the lanthanum chloride solution would change the pH of the solution, especially in the immediate

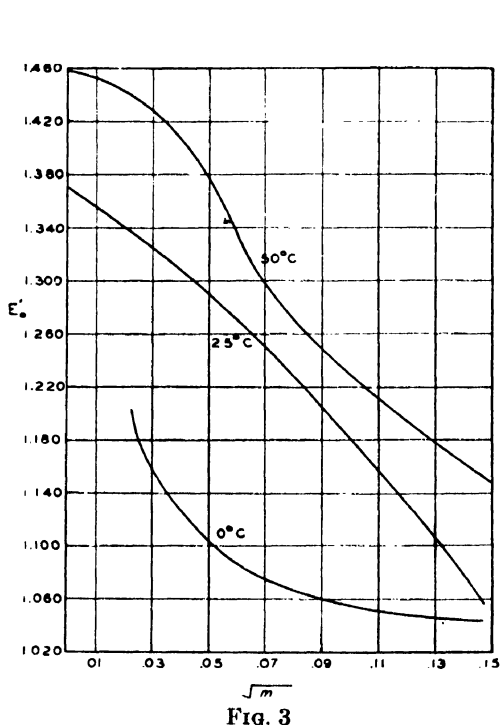


FIG. 3

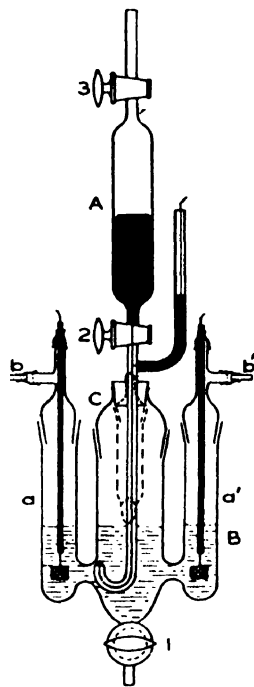
FIG. 3. Plot of values for E'_0 against the square root of the concentration

FIG. 4

FIG. 4. Electrode vessel

area of the amalgam, from 5.7 to 8.0 or slightly above. This was followed over a longer period of time by a slight evolution of hydrogen. Neither one of these processes could be brought about without hydrolysis, and in the cell would definitely cause interference with the cell process. It was necessary to abandon the use of aqueous solutions and endeavor to find a suitable non-aqueous solvent for lanthanum chloride.

ORGANIC SOLVENTS

The solubility of lanthanum chloride was determined in various organic solvents. To 25 cc. of the solvent 3 g. of lanthanum chloride was added

and the solution refluxed for 15 minutes. The solution was then filtered and the filtrate evaporated in a Pyrex dish. The residue, if any, was weighed. The results obtained are tabulated in table 3. Upon examination of these data it is seen that the solvents for lanthanum chloride fall into two definite groups: first, the aliphatic alcohols, and second, the aromatic tertiary amines. Acetone appears to be an exception to this rule. However, the solvent action of acetone is attributed to the difficulty of

TABLE 3
Solubility of lanthanum chloride in various organic solvents

SOLVENT	SOLUBILITY	
	<i>grams per liter</i>	
1,4-Dioxane.....	Insoluble	
Tributylamine.....	Insoluble	
Nitrobenzene.....	Insoluble	
Acetone.....	Slightly soluble	
Benzene.....	Insoluble	
Dibenzylamine.....	Insoluble	
Aniline.....	Insoluble	
Chloroform.....	Insoluble	
Carbon tetrachloride.....	Insoluble	
Quinoline.....	Slightly soluble	
Piperidine.....	Insoluble	
Pyridine.....	Very soluble	
Chlorobenzene.....	Insoluble	
Pyrrolidine.....	Soluble	
Furfuran.....	Too low boiling point	
Ether.....	Insoluble	
Ethyl alcohol.....	Very soluble	
<i>n</i> -Propyl alcohol*.....	300 ^{20°}	425 ^{40°}
Ethylene glycol*.....	166 ^{20°}	450 ^{40°}
Glycerol*.....	50 ^{30°}	150 ^{40°}

* Private communication from Professor B. S. Hopkins.

removing the last traces of water. Different samples of acetone gave varying results.

Apparatus

In the work with organic solvents the apparatus was reconstructed as shown in figure 4. Since purification of large volumes of organic solvents is cumbersome and sometimes difficult, the new cell had a capacity of only 30 cc. The cell vessel, B, had only two side arms, a and a', fitted with interchangeable ground-glass joints which were drawn down to small diameter to form a close fit with the reference electrodes. The top of each side arm contained a tube, b and b', which was used for passing nitro-

gen into the apparatus. The dropping electrode had a total capacity of 15 cc. It was held in place by a small stopper that fitted into an interchangeable glass joint. The glass joints made the assembling of the cell much easier and more rapid; this decreased evaporation and also the accumulation of impurities. The operating technique of the cell was similar to that of the original.

Alcohol cell

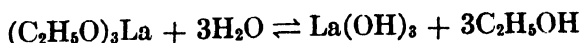
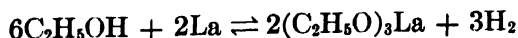
As one of the classes of solvents for lanthanum chloride was aliphatic alcohols, this type was first investigated by using ethyl alcohol. Since water interferes with the cell reaction, anhydrous conditions were necessary throughout. Both anhydrous lanthanum chloride and absolute alcohol were prepared. The preparation of anhydrous lanthanum chloride by the dehydration of $\text{LaCl}_3 \cdot 7\text{H}_2\text{O}$ was impossible, owing to the formation of the insoluble basic chloride (18). Therefore, it was necessary to seek some other method. Several were tried; the most satisfactory is that proposed by Reed, Hopkins, and Audrieth (23). Ten grams of lanthanum oxide was heated with 15 g. of ammonium chloride in a glass bulb to 250°C . This temperature was maintained and the excess ammonium salt removed by pumping in an all-glass apparatus. However, the anhydrous chloride prepared in this way, contrary to the statement of Reed, Hopkins, and Audrieth (23), does not give a clear solution in water. The salt was dissolved in absolute alcohol, and the insoluble material removed by centrifuging. This solution was diluted to the correct concentration and introduced into the cell.

The absolute alcohol was prepared by treating c.p. absolute alcohol with sodium metal and distilling slowly from an efficient column 120 cm. long. The first and last 150-cc. portions of the alcohol were discarded.

E.M.F. measurements were made on the cell,



The same shift in the E.M.F. was encountered here as in the aqueous cell. However, the maximum was reached in much less time, usually only 15 to 20 seconds being required. This made reading the cell very difficult and the results not very reproducible. Upon investigation it was found that hydrolysis was taking place, even though extreme care had been taken to obtain anhydrous conditions. The pH of the solution would change slowly over a period of three to four hours when in contact with lanthanum amalgam. Probably the following reactions took place:



This type of cell with the aliphatic alcohols as solvent was discarded on this evidence. If ultimately absolute conditions were obtained, the cell would still offer side reactions in that the lanthanum would replace hydrogen from the alcohol.

Aromatic tertiary amine cell

The second class of solvents for lanthanum chloride was that of aromatic tertiary amines. The one most easily purified and most readily obtained was pyridine. It also dissolves the lanthanum chloride to the greatest degree, thereby being useful over a wider concentration range. Double salts of the rare-earth salts and tertiary amines are reported (3, 12). However, double-salt formation is not particularly undesirable. The formation of complexes of the Werner type is not likely to occur, since lanthanum salts do not form complex compounds with ammonium hydroxide.

The pyridine was purified by distillation and then treated with 100 g. of activated aluminum oxide for every 500 cc. of pyridine. After standing for 24 hours the mixture was distilled twice, and the fraction boiling at 115.3°–115.5°C. was collected (1).

When the cell was set up it was found that pyridine dissolved the silver chloride from the reference electrode. It was necessary either to find a silver halide that would not dissolve in pyridine or to saturate the pyridine with the silver halide and find the correction to be applied. If we draw an analogy between the solubility of the halides of silver in ammonium hydroxide and what we should expect to find in pyridine, we should look for a lower solubility of the iodide, the solubility increasing to the chloride. The only reference in the literature was that of Laszczynski (15), who reports the solubility of silver iodide as 0.1 g. per 100 grams of pyridine at 10°C. and 8.01 g. at 121°C. The solubility of silver chloride was found to be 1.9 g. per 100 grams of pyridine at 25°C., a value that appeared to be greater than the solubility of the iodide at the same temperature. The silver-silver bromide electrode was prepared by the method of Lewis and Storch (17), and the iodide electrode by a procedure outlined by Jones and Hartman (10). The iodide cell could not be investigated, because it was found impossible to prepare anhydrous lanthanum iodide.

Since the chloride cell offered the smallest correction factor we attempted to saturate some pyridine with silver chloride and then dissolve lanthanum chloride in this solution to the desired concentration. Unfortunately, the mercury of the amalgam replaced the silver chloride dissolved in the pyridine and precipitated metallic silver. From this evidence it was necessary to discard any combination where pyridine and the halide reference electrodes were used together. The same objection held in the case of pyrrolidine and quinoline.

The possibility of a lead-lead sulfate or mercury-mercurous sulfate reference electrode led to the preparation of lanthanum sulfate and an investigation of its solubility in organic solvents. The lanthanum sulfate was prepared by dissolving lanthanum oxide in an excess of sulfuric acid, from which it crystallizes in the form of $\text{La}_2(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$ when the solution is cooled. It may be dehydrated by heating to 150°C . for 4 hours. There was no organic solvent found that would dissolve this anhydrous lanthanum sulfate.

The results of this investigation definitely prove that an E.M.F. method involving a lanthanum amalgam electrode is not applicable to the study of lanthanum salts without considerable difficulty. Some other method such as vapor-pressure or freezing-point measurements should be used even though they are not very satisfactory in dilute solutions.

SUMMARY

1. A dropping electrode apparatus was constructed for use with the very active lanthanum amalgam in electrochemical cells.

2. The electromotive force of the cell $\text{La}(\text{satd. amalgam})-\text{LaCl}_3(\text{H}_2\text{O})-\text{AgCl}-\text{Ag}$ was investigated at 0° , 25° , and 50°C . for concentrations of lanthanum chloride of 0.0005, 0.001, 0.002, 0.003, 0.005, 0.011 and 0.022 molal.

3. The solubility of lanthanum chloride was investigated in various organic solvents.

4. The following electrochemical cells were also investigated:

$\text{La}(\text{satd. amalgam})-\text{LaCl}_3(\text{ethyl alcohol})-\text{AgCl}-\text{Ag}$

$\text{La}(\text{satd. amalgam})-\text{LaCl}_3(\text{pyridine})-\text{AgCl}-\text{Ag}$

$\text{La}(\text{satd. amalgam})-\text{La}_2(\text{SO}_4)_3(\text{H}_2\text{O})-\text{Hg}_2\text{SO}_4-\text{Hg}$

5. In all cells where water served as the solvent the E.M.F. was disturbed by the hydrogen overvoltage on lanthanum. A similar reaction occurred when aliphatic alcohols were employed. In cells involving tertiary aromatic amines there was a large solvent action on the reference electrode which could not be corrected for in the customary manner.

6. From this investigation it is definitely concluded that lanthanum amalgams are unsatisfactory for precise E.M.F. measurements.

We wish to express our thanks to the National Research Council for a Grant-in-aid which in part made possible the construction of the apparatus used in this investigation.

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THE DISTRIBUTION OF SOLUTES IN SILICA GEL¹

SUTTON REDFERN² AND W. A. PATRICK

Department of Chemistry, The Johns Hopkins University, Baltimore, Maryland

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It has been shown that within a hydrogel of silicic acid a solute is associated with a greater quantity of water than outside the hydrogel. If the concentrations are expressed as molalities, then it is found that the concentration inside the gel is less than the concentration outside. This conclusion was reached on the basis of the experimental studies of the diffusion of electrolytes in hydrogels by Allan (1) and the analytical studies of Love (7). These papers gave results for sodium sulfate and hydrochloric acid.

Allan and Love were also led to believe that the activity coefficient of the solute in the gel was different from the activity coefficient outside, since the activities at equilibrium must be equal. However, this conclusion is based on the assumption that all of the water in the gel is acting in the rôle of solvent. This is probably not true, because there is considerable evidence for the existence of what is called bound water. The hydration of molecules or ions in solution is one example. Substances such as gelatin, gum arabic, silica gel, and alumina have the property of adsorbing water. This water does not exhibit its normal vapor pressure or other colligative properties. Neuhausen and Patrick (11) have shown that a silica gel can be heated to 300°C. in a vacuum produced by a Gaede pump for a period of 6 hours without reducing the water content below 4.8 per cent. In recent years the extensive series of measurements of bound water initiated by the studies of Newton and Gortner (12) on bound water in plant saps leave little doubt that such a thing as bound water exists.

A satisfactory, absolute definition of bound water has never been made. Briggs (2) says that "there are nearly as many definitions of bound water as there are methods for determining it. The methods are consistent in that they remove or otherwise change the state of a fraction of the water leaving a portion unaccounted for, this being designated as bound. The

¹ This article is based upon the dissertation submitted by Sutton Redfern to the Faculty of Philosophy of the Johns Hopkins University in partial fulfillment of the requirements for the degree of Doctor of Philosophy, 1936.

² Present address: The Fleischmann Laboratories, 810 Grand Concourse, New York, New York.

usual idea of bound water carries with it a picture of a portion of the water in the system as being associated with the colloid phase with such strength that it is no longer free to exhibit those properties which are characteristic of water, i.e. it is no longer available to act as a solvent, or it cannot be separated from the colloid by freezing it or by subjecting the system to pressure, as in an ultrafilter."

Very probably there is a definite bound water \rightleftharpoons free water equilibrium which is measured at a different point in each different method. This makes it difficult to get check results, although Sayre (15) has obtained check results by three different methods on a gum arabic sol.

The purpose of this study is to test accurately the whole question from an experimental standpoint, and furthermore to formulate if possible a rational explanation of the phenomena involved.

BRIEF STATEMENT OF METHOD

The method of studying the distribution of the various solutes between the gel and its surrounding equilibrium solution is in brief as follows: A cylinder of silica gel, of previously determined water content, was placed in a flask with the desired solute solution; the flask was placed in the thermostat and allowed to stand, with occasional shaking, for two weeks or longer. Then duplicate samples of the external solution were removed to tared weighing bottles, and the molal concentration of the solute determined by the appropriate method. The gel was removed from the solution and carefully wiped with filter paper to remove any excess solution. Four samples of the gel were then cut off and the silicon dioxide content of two of them and the solute content of the other two were determined. The above analyses gave sufficient data from which the concentration of solute in the gel and the concentration of solute in the external solution could be calculated.

PREPARATION OF GELS

Gels prepared from sulfurous acid (1) have a greater mechanical strength than gels prepared from sulfuric or hydrochloric acids and so were used. The sodium silicate used to prepare the gels was a commercial product containing Na_2O and SiO_2 in the ratio 1:3.51. It was diluted until it contained 6 per cent Na_2O . The gels were prepared by adding the diluted sodium silicate solution to a saturated aqueous solution of sulfur dioxide and pouring the resulting sol into paraffined glass molds 3.4 x 10 cm. After the sol set to a gel, it was removed and washed overnight in tap water in order to remove most of the soluble salts. The gel cylinders were then washed alternately in 6 *N* and 12 *N* hydrochloric acid until no more iron was extracted, and finally washed in distilled water until free of chloride. Gels washed in this manner with hydrochloric acid did not

contain more than 0.1 per cent residue based on the weight of silica after the silica was removed with hydrofluoric acid and sulfuric acid.

After being washed, the gels were dried superficially in the open air. They were now approximately 85 per cent water and could be used directly as representing this water content. For lower water contents, the gel cylinders were dried slowly under raised bell jars. The drying process was followed by weighing the cylinders. Since these dried gels would crack when placed in water, they were resaturated with water vapor by Allan's method (1).

EQUILIBRATION AND SAMPLING OF GELS

The solutes used in this investigation were potassium chloride, potassium bromide, sodium chloride, sodium bromide, lithium chloride, magnesium chloride, barium chloride, calcium chloride, strontium chloride, and dextrose. These solutes were all of C.P. grade and were used without further purification.

A gel cylinder was placed in a 250-ml. wide-mouth Erlenmeyer flask and covered with a solution of the solute. The flask was tightly stoppered with a rubber stopper, placed in a thermostat maintained at $25.00^{\circ}\text{C} \pm 0.05^{\circ}$, and left for two weeks or longer. The dextrose solutions were covered with a layer of toluene to prevent the formation of mold. It is a safe assumption that the toluene did not interfere. Jones and Gortner (5) also used toluene "because of its inactivity towards aqueous colloidal systems." When the gel had come to equilibrium, duplicate samples of the external solution were removed, weighed, and the amount of dissolved solute determined. The gel cylinder was then removed and immediately wiped off carefully with filter paper. Two samples of gel were then broken off with a knife and placed in weighing bottles. The silica was determined in these samples. The rest of the gel was split into two pieces, and the solute removed and analyzed by an appropriate method.

METHODS OF EXTRACTION AND ANALYSIS

The gel samples were extracted in a Soxhlet extraction apparatus. When dextrose was extracted with boiling water, a slight decomposition took place. Therefore the extraction apparatus was modified so that it could be run under a constant reduced pressure of 80 mm. of mercury. The lowered boiling point prevented decomposition. Difficulty was experienced with bumping under the reduced pressure, so a slow stream of nitrogen was introduced through a tube sealed through the side of the flask. A water pump supplied the necessary vacuum.

The Mohr method was used for the analysis of all the electrolytes except barium chloride; in this case the Volhard method was used. The dextrose was analyzed by the Quisumbing and Thomas (14) modification of Feh-

ling's method. Silica was determined by the Willard and Cake (20) perchloric acid method. It was not necessary to go through this procedure for the samples containing dextrose. In this case the gel was weighed directly into a platinum crucible and ignited.

The initial water content of each gel cylinder was determined before it was placed in the solution. Duplicate samples of the resaturated gel were removed from each end of the cylinder, placed in platinum crucibles, and ignited.

CALCULATIONS

The analysis of the equilibrium solution and the gel gave the following ratios:

$$A = \frac{\text{Solute}}{\text{H}_2\text{O in solution}} \quad B = \frac{\text{Solute}}{\text{Gel}} \quad C = \frac{\text{SiO}_2}{\text{Gel}}$$

These ratios, of course, are expressed as grams per gram. By calculation the following ratios were obtained:

$$D = \frac{\text{H}_2\text{O}}{\text{Gel}} = 1 - (B + C) \quad E = \frac{\text{Solute}}{\text{H}_2\text{O in gel}} = \frac{B}{D} \quad \Delta = A - E$$

The Δ is the difference between the concentration outside and inside and is found to be always positive.

If the free water of the system is defined as the fraction of the total water which is acting as a solvent and gives a solution inside the gel of the same concentration as the surrounding equilibrium solution, then the bound water is defined as the difference between the total water and the free water. In general, all methods for determining bound water depend on the determination of the total and free water, and define the bound water by difference.

In order to apply the above definition, let X = the number of grams of bound water in 1 g. of gel. Then must

$$\frac{B}{D - X} = A$$

or

$$\frac{X}{D} = \frac{A - E}{A} = \frac{\Delta}{A}$$

but X/D is the fraction of the total water which is bound. However, a better expression of the amount of bound water is to give the number of grams of bound water per gram of silica. This ratio, called W , is given by

$$W = \frac{D \cdot \Delta}{C \cdot A} = \frac{\text{grams H}_2\text{O}}{\text{grams SiO}_2}$$

In order to see whether there was any correlation between the activity of the water in the equilibrium solution and the amount of bound water, the activity of the water in the different solutions was calculated from the activity coefficients of the solute by the following formula:

$$-\log a_{(m_1)} = \frac{m_1 \nu}{127.84} + \frac{\nu}{55.51} \int_0^{m_1} m \, d \log \gamma$$

where $a_{(m_1)}$ = activity of water when the molality of the solute is m_1 ,

m_1 = molality of solute,

ν = total number of ions formed from solute, and

γ = activity coefficient of solute.

TABLE 1
85 per cent gel series

SOLUTE	WATER CONTENT OF GEL	MOLALITIES OF EQUILI- BRUM SOLUTION	Δ	BOUND WATER IN GRAM PER GRAM OF SiO ₂	ACTIVITY OF WATER	RATIO A/E
MgCl ₂	86.79	0.4231	0.00215	0.302	0.981	1.056
CaCl ₂	86.72	0.3990	0.00187	0.273	0.981	1.044
SrCl ₂	86.66	0.4043	0.00314	0.320	0.981	1.052
BaCl ₂	86.33	0.4190	0.00438	0.318	0.981	1.053
NaCl.....	86.89	0.8322	0.00168	0.231	0.973	1.036
NaBr.....	87.00	0.8264	0.00309	0.239	0.972	1.038
LiCl.....	88.29	0.8260	0.00107	0.228	0.971	1.032
KBr.....	88.22	0.8324	0.00253	0.187	0.973	1.026
KCl.....	84.06	0.8273	0.00181	0.160	0.974	1.030
KCl.....	84.06	0.4033	0.00095	0.175	0.987	1.033
Dextrose.....	82.68	0.8656	0.00660	0.201*	0.985	1.044
Dextrose.....	85.16	0.4227	0.00357	0.272	0.992	1.049

* These results deviate from the general rule that the amount of bound water decreases as the silica content of the gel increases.

By plotting m against $\log \gamma$, the last integral can be graphically integrated. The necessary values of the activity coefficients were taken from the Landolt-Börnstein (6) tables. The coefficients for magnesium chloride were at the freezing point of the solution, but it was assumed that these were not greatly different from the values at 25°C. The curves were carefully plotted and integrated with a polar planimeter. In the case of the dextrose solutions the activity of the water was calculated from the measurements of Morse (9) on the osmotic pressures of dextrose solutions.

DATA

All of the data on the gels can be conveniently divided into three groups, depending on the approximate initial water content of the gel. The three

groups are designated as the 85 per cent gel series, the 70 per cent gel series, and the 50 per cent gel series. Tables 1, 2, and 3 give the results

TABLE 2
70 per cent gel series

SOLUTE	WATER CONTENT OF GEL	MOLALITIES OF EQUILI- BRIUM SOLUTION	Δ	BOUND WATER IN GRAMS PER GRAM OF SiO ₂	ACTIVITY OF WATER	RATIO A/E
MgCl ₂	73.02	0.5149	0.00444	0.263	0.973	1.100
CaCl ₂	72.16	0.4557	0.00469	0.257	0.976	1.102
SrCl ₂	71.35	0.4625	0.00818	0.300	0.978	1.126
BaCl ₂	63.76	0.4864	0.01420	0.272	0.977	1.163
NaCl.....	72.40	0.9616	0.00441	0.218	0.968	1.085
NaBr.....	72.24	0.9422	0.00867	0.246*	0.968	1.098
LiCl.....	65.73	0.9642	0.00395	0.204*	0.966	1.107
KBr.....	67.15	0.9671	0.00980	0.178	0.969	1.093
KCl.....	65.93	0.9582	0.00477	0.141	0.970	1.072
KCl.....	70.94	0.4718	0.00267	0.197*	0.985	1.082
Dextrose.....	69.01	1.007	0.01660	0.210	0.982	1.101
Dextrose.....	72.84	0.4723	0.00712	0.233	0.992	1.091

* These results deviate from the general rule that the amount of bound water decreases as the silica content of the gel increases.

TABLE 3
50 per cent gel series

SOLUTE	WATER CONTENT OF GEL	MOLALITIES OF EQUILI- BRIUM SOLUTION	Δ	BOUND WATER IN GRAMS PER GRAM OF SiO ₂	ACTIVITY OF WATER	RATIO A/E
MgCl ₂	50.69	0.5052	0.01062	0.240	0.974	1.283
CaCl ₂	55.21	0.4741	0.00833	0.204	0.975	1.188
SrCl ₂	54.04	0.4877	0.01575	0.256	0.977	1.256
BaCl ₂	54.10	0.4888	0.02010	0.244	0.977	1.246
NaCl.....	54.62	0.9996	0.00933	0.202	0.967	1.190
NaBr.....	54.19	0.9912	0.01620	0.198	0.966	1.189
LiCl.....	55.88	0.9800	0.00653	0.208	0.965	1.186
KBr.....	54.61	0.9990	0.01440	0.150	0.968	1.138
KCl.....	55.46	0.9962	0.00776	0.135	0.968	1.117
KCl.....	55.31	0.4899	0.00420	0.155	0.984	1.130
Dextrose.....	53.78	1.056	0.03450	0.205	0.981	1.222
Dextrose.....	52.94	0.5033	0.01670	0.212	0.991	1.226

for the respective series. Calculations were also made assuming that the dextrose molecule is monohydrated in solution. It was found that the formation of a monohydrate increases the difference in concentrations

outside and inside. These calculations are not tabulated, because the only evidence for the hydration of dextrose is the fact that dextrose forms a crystalline monohydrate. Sucrose in dilute solutions forms a hexahydrate (16), and Newton and Gortner (12) always corrected their freezing-point measurements by assuming the formation of the sucrose hexahydrate.

The accuracy of the determinations is as follows: In the determination of the water content of the gels, the maximum deviation from the mean was ± 0.5 per cent. The deviation from the mean of ratio *A* was ± 0.2 per cent; of ratio *B*, ± 1.0 per cent; and of ratio *C*, ± 0.75 per cent. It is therefore believed that the results are accurate to at least ± 2.0 per cent.

DISCUSSION

According to a tentative theory of one of the authors, it was originally expected that the dextrose would be equally distributed. This expectation was pointed out to Dr. I. Langmuir in the spring of 1935; he immediately suggested that the electrolytes showed a difference because the dielectric constant inside the gel was different from that in the outside solution. This would mean a difference in the electrical energy of the ions and a Boltzmann distribution would result. However, the experimental results showed that this suggestion was not the explanation. Furthermore, the idea that the dielectric constant of the largest fraction of the water in the gel is different from the water outside is probably not true. Marinesco (8) measured the dielectric constant of aqueous solutions of hydrophilic colloids, and by application of the dipole theory of Debye determined the quantity of water fixed by these colloids. In effect free water has a dielectric constant of 80, while in the water which is bound by colloids the molecular dipoles are blocked and can no longer lead to polarization, so that the dielectric constant is now no more than of the order of 2 to 3. Other evidence for a lower dielectric constant of the bound water is to be found in the literature (10, 17, 18, 19).

The calculations made on the assumption of bound water show definite qualitative trends, although no quantitative results can be deduced from the present set of measurements. The data show that in all cases except four, which are starred, the amount of bound water decreases as the silica content of the gel increases. This decrease is easily explained qualitatively. The gel cylinders when dried shrink considerably in volume and this shrinkage is irreversible. Therefore the gels of lower water content have a smaller internal volume, which means less surface for the layer or layers of bound water; consequently there is less bound water per gram of silica.

The same results were found for gelatin gels and sols by Jones and Gortner (5) using the dilatometric method and by Newton and Martin (13) using the cryoscopic method. In the gelatin-water system, however,

the water binding appears to be an adsorption reaction, because a logarithmic relationship was found to exist between the concentration of the gelatin gel and the grams of water which were bound per gram of dry gelatin. An attempt was made to plot the present results on log-log coördinate paper, but the measurements did not give a straight line.

Briggs (2) found that the amount of bound water associated with the colloid varied with the activity of the water. The higher the activity of the water, the greater the quantity of bound water. Measurements of the gum arabic-water systems with the cryoscopic technique showed that different solutes gave a smooth curve of water content against water activity.

The results on silica gel do not show any such simple relations. For example, an examination of the results for magnesium chloride, calcium chloride, strontium chloride, and barium chloride in the 85 per cent gel series shows different values for the amount of bound water, although the activity of the water is the same for each salt. The water contents of the different gels are sufficiently close to remove this variable. However, in the case where the same solute was used, potassium chloride or dextrose, the bound water is greater the greater the activity of the water. Apparently Briggs' statement—"At any given activity of the water in a system in which colloids and crystalloids are in equilibrium, provided the various non-water components have not reacted with each other upon mixing, the amount of water associated with or bound by a given weight of any of the non-water components will always be the same, and it will be the same as that which the given weight of the component will be associated at the same water activity when it is the only non-water component in equilibrium with water."—is not true for the silica systems.

It was thought that perhaps a Donnan equilibrium was responsible for the unequal distribution. The Donnan equilibria are characterized by the presence in a system of electrolytes of a species of ion which is restrained in *any* way from diffusing to all parts of the system, and this gives rise to unequal distribution of every species of diffusible ion present. These equilibria are immediately thrown out because of the experimentally determined unequal distribution of dextrose, and also because the same distribution would be expected for all the uni-univalent chlorides and the same for all the bi-univalent chlorides; the latter is found not to be true. Furthermore, it is hard to find the restraint necessary for the distribution.

Adsorption also will not explain the results. Grettie and Williams (4) found that even activated silica, i.e., silica which had been heated to 120° C. for several hours, only adsorbed dextrose to the extent of 0.7 per cent. The silica gel used in the present experiments was certainly not activated and would be expected to show no adsorption. However, adsorption is in the opposite direction to that which was actually found. If the gel does adsorb chloride ions, as was found by Ganguly and Krishnamurti (3)

for a silica sol prepared from silicon tetrachloride, then this would also produce the opposite effect, namely, a greater concentration inside the gel than outside.

It is frankly admitted that at present the authors cannot suggest a reasonably satisfactory explanation of the results described herein.

SUMMARY

1. A study has been made of the distribution of potassium chloride, potassium bromide, sodium chloride, sodium bromide, lithium chloride, magnesium chloride, calcium chloride, strontium chloride, barium chloride, and dextrose between a hydrogel of silicic acid and the surrounding equilibrium solution.

2. In all cases the molal concentration of solute inside the gel was found to be less than the molal concentration outside.

3. Calculations made on the assumption that part of the water was not acting as a solvent but was bound water showed that the amount of bound water decreased as the silica content of the gel increased.

4. No correlation was found between the activity of the water and the quantity of bound water.

5. The results could not be explained satisfactorily on the basis of bound water, adsorption, or Donnan equilibria.

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SUGAR ALCOHOLS. X

THE EFFECT OF CERTAIN SUGAR ALCOHOLS AND THEIR ANHYDRIDES ON THE DISSOCIATION OF BORIC ACID

FREDERICK K. BELL, C. JELLEFF CARR, WILLIAM E. EVANS, AND
JOHN C. KRANTZ, JR.

*Department of Pharmacology, School of Medicine, University of Maryland,
Baltimore, Maryland*

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INTRODUCTION

In previous communications the authors (7, 8) have studied the influence of various sugar alcohols and their anhydrides on the dissociation of boric acid. Later the physicochemical properties of the erythritan-boric acid complex were studied (9). For the metabolism work carried out in this laboratory several more sugar alcohols, anhydrides, and other related compounds have been prepared for study. The availability of these substances prompted a further extension of the work on the dissociation of boric acid.

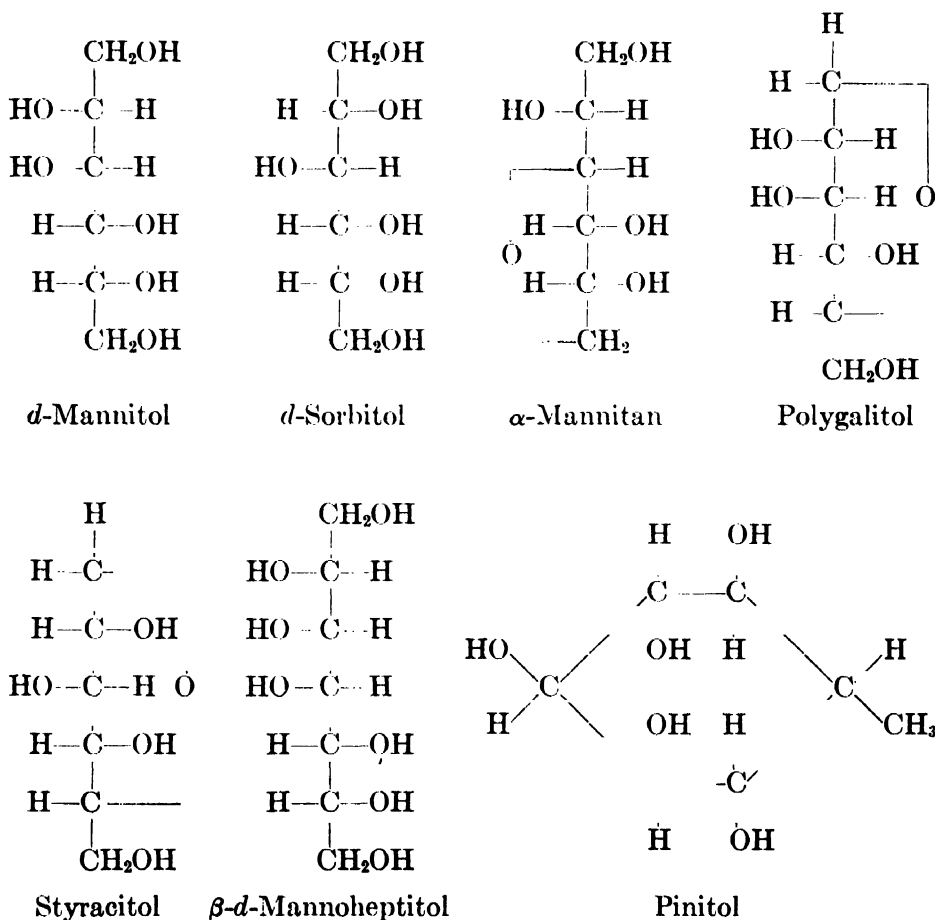
MATERIALS AND METHOD

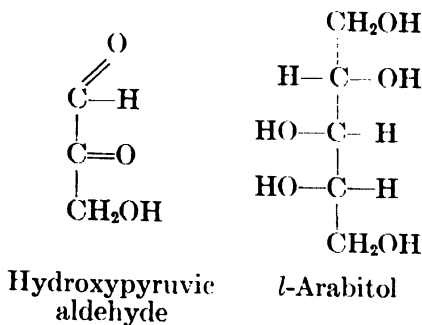
The boric acid was of buffer quality. The mannitan was prepared from mannitol by a slight modification of the method of Vignon (13), in which the dehydration is accomplished by means of sulfuric acid. Analysis gave the following values: carbon, 44.08 per cent; hydrogen, 7.04 per cent. The calculated values are: carbon, 43.90 per cent; hydrogen, 7.32 per cent. The α -mannitan was prepared by the method of Bouchardat (5), in which mannitol is dehydrated by boiling with hydrochloric acid. The compound melted between 139° and 140°C. (uncorrected); the value found for its specific rotation, $[\alpha]_D^{20}$ was -22.0° . The polygalitol was extracted from *Polygala amara* (4). The compound melted between 142° and 143°C. (uncorrected); $[\alpha]_D^{16} = +47.8^\circ$. The styracitol was prepared by the reduction and hydrolysis of tetraacetyloxyglucal by the method of Zervas (15). The compound melted at 157°C. (uncorrected). The β -*D*-mannoheptitol was extracted from *Primula officinalis* by the method of Bougault and Allard (3). The compound melted at 153°C. (uncorrected). The pinitol was extracted by the method of Sherrard and Kurth (10), from *Pinus libertiana* which was kindly supplied by C. L. Hill of the U. S. Department

of Agriculture. The purified compound melted between 183° and 185°C. The hydroxypyruvic aldehyde was prepared by a modification of Evans' method (5). The nitrogen content of its dioxime was 23.40 per cent. The calculated value is 23.73 per cent. The *l*-arabitol was Pfanstiehl's c.p. product. The sorbitol and mannitol were kindly supplied through the courtesy of the Atlas Powder Co. of Wilmington, Delaware.

Solutions of the various compounds studied contained 4 g. of the compound in 100 cc. of 0.1 molar boric acid. Stronger concentrations were employed for conductivity measurements. To 10-cc. portions of this solution was added 0.1 normal sodium hydroxide in quantities varying from 1 cc. to 12 cc. Immediately after the addition of the alkali the pH of the solution was determined electrometrically at 25°C. $\pm 0.5^\circ$, using the Wilson type hydrogen electrode (14).

The following formulas indicate the structural relationship existing among the compounds.





Recent work by Freudenberg and Rogers (6) indicates that the structure of styracitol is that which was assigned formerly to polygalitol and *vice versa*.

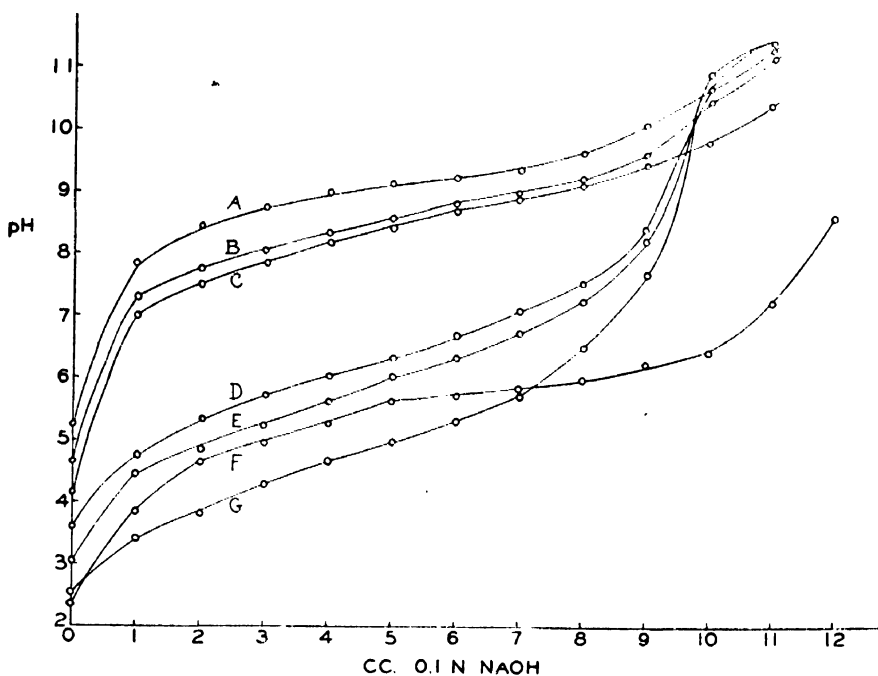


FIG. 1. The effect of sugar alcohols on the dissociation of boric acid. Curve A, *M*/10 boric acid; curve B, styracitol, polygalitol, and pinitol; curve C, syrupy mannan; curve D, *l*-arabitol; curve E, β -*d*-mannoheptitol and sorbitol; curve F, hydroxypyruvic aldehyde; curve G, α -mannan.

The results of pH measurements are set forth in figure 1.

DISCUSSION

There are many features of interest that may be gleaned from a study of figure 1. First, the heptahydric alcohol β -*d*-mannoheptitol is no more

effective in its downward displacement of the titration curve of boric acid than its hexahydric homologues, mannitol and sorbitol; the curves of these three boric acid complexes practically coincide. Second, the slight potentiation of the dissociation constant of boric acid by styracitol, 1,5-anhydrosorbitol, is identical with that produced by its epimer polygalitol, 1,5-anhydromannitol. Third, pinitol, monomethylinositol, is quite as ineffective in potentiating the dissociation of boric acid as is its homologue, *i*-inositol, studied previously by the authors.

Further, the extraordinary titration curve of the hydroxypyruvic aldehyde-boric acid complex requires special comment. This extremely labile substance forms a complex with boric acid, as evinced by the greater degree of hydrogen-ion concentration conferred upon the boric acid solution by the addition of hydroxypyruvic aldehyde. However, one equimolecular weight of alkali was not sufficient to neutralize the complex, and at the boric acid-alkali equimolar point the pH of the solution was 6.45. We attribute this to the enolization of hydroxypyruvic aldehyde with the resulting increased alkali-consuming power. After the solution became alkaline (pH = 8.64) upon the addition of sodium hydroxide (12 cc. of *N*/10), drifting potentials were obtained with the hydrogen electrode.

The action of *l*-arabitol on the acidity of boric acid is especially interesting. One would expect, according to the Böeseken (12) hypothesis, that this substance, having two hydroxyl groups on the same side of adjacent carbon atoms, would cause a very strong downward displacement of the titration curve of boric acid. Its effect was, however, less marked than that of mannitol or sorbitol and far less pronounced than that of α -mannitan. The extraordinary effects of syrupy mannitan and of α -mannitan require special comment. In concentrations in which syrupy mannitan exhibited a pH of 4.20 (7) the α -mannitan boric acid complex gave a pH of 2.56. The syrupy mannitan employed by the authors therefore showed a value quite different from Böeseken's value. Böeseken, in conference with one of the authors (J. C. K., Jr.) in The Hague, suggested that our values showed a lesser degree of potentiation of the dissociation of boric acid because of the contamination of syrupy mannitan with isomannide. Isomannide is known to be ineffective. In testing this hypothesis, it was found that isomannide as such had no interfering effect on the potentiation of the dissociation constant of boric acid by mannitan. Furthermore, with α -mannitan known to be isomannide-free, the removal of as much as 20 per cent of the α -mannitan and its replacement with isomannide changed the original pH of 2.56 to only 2.70. The combustion analysis data preclude the probability of the presence of more isomannide. Therefore this hypothesis does not account for this difference in response.

To investigate this problem further conductivities of various sugar alcohol-boric acid complexes were measured. These results are shown in

table 1. The effect of dilution on the α -mannitan-boric acid complex is shown in figure 2.

TABLE 1
Specific conductivities
Aqueous solutions at 25°C.; cell constant = 0.1444

SOLUTION	SPECIFIC CONDUCTIVITY
	<i>mhos</i>
0.5 M H_3BO_3	32.9×10^{-6}
0.5 M H_3BO_3 + 0.2 M mannitol.....	357×10^{-6}
0.5 M H_3BO_3 + 0.2 M mannitan.....	959×10^{-6}
0.5 M H_3BO_3 + 0.2 M α -mannitan.....	939×10^{-6}
0.2 M α -mannitan.....	26×10^{-6}
0.2 M mannitan (second batch).....	1099×10^{-6}
0.5 M H_3BO_3 + 0.2 M polygalitol.....	42.9×10^{-6}
0.5 M H_3BO_3 + 0.2 M styracitol.....	46.0×10^{-6}

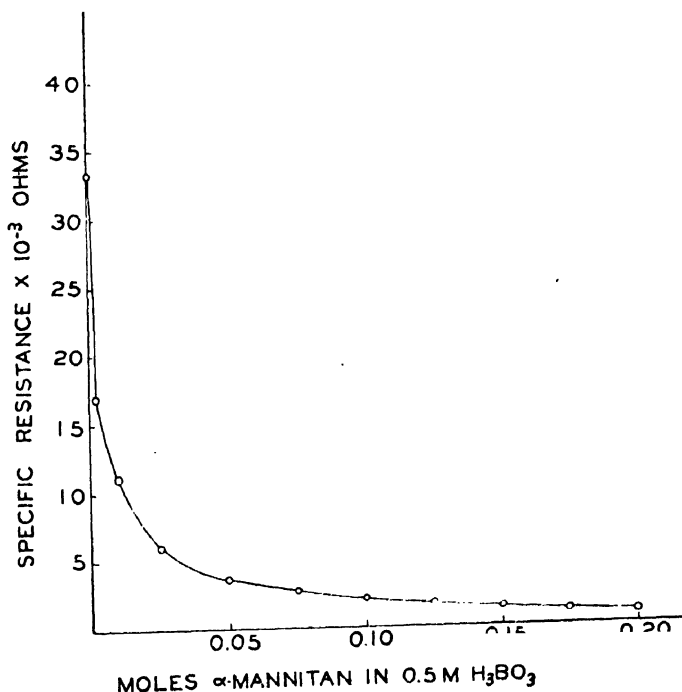


Fig. 2

Hydrogen-ion concentration measurements were made on the solutions on which conductivities were determined. The values were as follows: mannitol complex, pH 2.82; syrupy mannitan complex, pH 3.62; the α -

mannitan complex, pH 2.45. Thus there is apparently the anomalous situation of the mannitan-boric acid complex exhibiting a high conductivity and a relatively low hydrogen-ion concentration. A further examination of table 1 reveals, however, that the syrupy mannitan alone showed a conductivity comparable to that of its boric acid complex. This results from electrolytes present in the mannitan because they were incompletely removed during its purification. Although the authors have succeeded in preparing syrupy mannitan barium-free and sulfate-free, the compound invariably is contaminated with traces of the ammonium salt of the sulfonic acids of mannitol. Distillation *in vacuo* removes the sulfonate, but during the process most of the mannitan is converted into isomannide. Knowing that at best the syrupy mannitan is contaminated with sulfonated products, the authors are inclined to believe that the striking agreement in the conductivity of the mannitan-boric acid complexes was fortuitous. Further studies with different batches of mannitan supported this hypothesis.

van Romburgh and van der Berg (12) in their conductivity measurements of the mannitol and mannitan-boric acid complexes obtained values practically identical with those herein reported. They did not state whether the mannitan was syrupy or crystalline α -mannitan. The conductivity values for their mannitan exceeded the values reported here for α -mannitan. The structure assigned to mannitan by these investigators is that reported in this communication. Their conclusion was based on the fact that α -vinylidihydrofuran could be obtained from mannitan tetraformate by reduction with hydrogen. Further evidence to support this proposed structure was presented by Valentin (11), who showed that 3,6-anhydromannose reduced with sodium-mercury amalgam in weakly alkaline solution yielded 3,6-anhydromannitol, the constants of which are identical with those of the crystalline α -mannitan of Bouchardat. α -Mannitan is levorotatory, $[\alpha]_D^{20} = -22.0^\circ$, and syrupy mannitan is dextrorotatory, $[\alpha]_D^{20} = +33.7^\circ$: this, in addition to the different effects on the dissociation constant of boric acid, suggests different structures for these two compounds.

SUMMARY

1. The downward displacement of the titration curve of boric acid effected by styracitol, polygalitol, *l*-arabitol, β -*d*-mannoheptitol, pinite, and hydroxypyruvic aldehyde has been determined.

2. The heptahydric alcohol, β -*d*-mannoheptitol, shows no greater potentiation of the dissociation constant of boric acid than its hexahydric homologues, mannitol and sorbitol.

3. Extra-stoichiometric alkali-consuming power of the hydroxypyruvic aldehyde-boric acid complex was observed.

4. The quantitatively different displacements of the titration curve of boric acid by syrupy mannitan and α -mannitan are recorded and discussed.

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THE SOLUBILITY OF SILVER IN MERCURY. III

ROBERT J. MAURER

Department of Chemistry, The University of Rochester, Rochester, New York

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Systematic investigations of the solubility of silver in mercury have been reported by Joyner (3), Sumier and Hess (5), and DeRight (1). Since below 30°C. the results of DeRight were not in agreement with those of Joyner, and since DeRight encountered serious experimental difficulties in this region, the present work was undertaken in an attempt to extend below room temperature, by the use of a technique different from that of DeRight, the precise knowledge of the solubility of silver in mercury. The work has been interrupted and there is little possibility that it will be continued, but the data which have been collected are considered of sufficient value to warrant publication.

MATERIALS

The silver used was in the form of 1000 fine foil obtained from the U. S. Mint in Philadelphia. One portion of the mercury used was purified by dropping it five times through a five-foot Meyer tube containing 6 *N* nitric acid, washing three times with distilled water in the same fashion, and triple distilling under reduced pressure according to the method of Hulett and Minchin (2). The other portion of mercury used was obtained from the Taylor Instrument Company and was stated to have been triple distilled. The conditions of distillation were not specified. When evaporated according to the method of analysis the mercury left no weighable residue. Under the same conditions there was no detectable loss in weight of the silver. In some cases a mixture of silver foil and solid phase from previous runs was used in preparing the amalgam.

APPARATUS

Except in runs F and G, where a smaller thermostat was used, the thermostat was that used by DeRight (1). The temperature was automatically controlled by a mercury thermoregulator and electrical heating units. As read on a Beckmann thermometer, the thermostat temperature was constant to better than $\pm 0.02^{\circ}\text{C}$. Temperatures were read from a Hiergesell Bros. thermometer of the double diamond grade

to 0.02°C . This thermometer was calibrated against a thermometer certified by the Bureau of Standards.

EXPERIMENTAL

The apparatus for preparing the amalgams is shown in figure 1.

The amalgams were prepared by placing an excess of silver in contact with mercury in flask A suspended in the thermostat. The mixture was agitated by a stirrer, and after a given length of time the liquid phase was drawn off by lowering the sintered glass filter C, making connection, by means of the rubber stopper D, to a flask which could be evacuated. The thermostat temperature was always below room temperature. The filter was model 154 G-1, made by Schott and Jena, with a pore size of from 100 to 120 microns, according to the makers. With such a filter, 200 cc. of

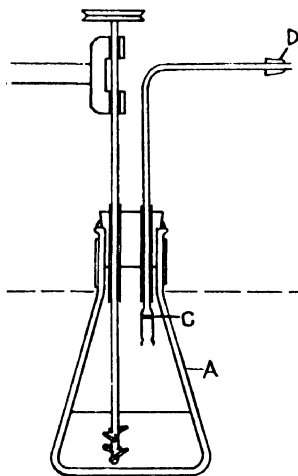


FIG. 1. The apparatus for preparing the amalgams

amalgam could be drawn off in a few minutes. The liquid phase was separated into samples which were analyzed according to the method described by DeRight (1). It should be noted that the procedure here used differed from that of DeRight (1) and Sunier and Hess (5) in that each sample which they analyzed represented a separate solubility determination. The weights used were calibrated and compared with a weight certified by the Bureau of Standards.

Table 1 shows the results of a check run upon an unsaturated amalgam. Some difficulty was experienced in run A in bringing the silver residues to constant weight, using several short periods of heating (5 hours) at 500°C . in a stream of hydrogen. In all succeeding runs, after evaporation of the mercury the residues were heated continuously for 50 hours or more at 500°C . in a stream of hydrogen. The residues then showed no change in

weight on further heating. The rather large deviation (5.8 parts per thousand) between the known and measured atomic per cent of silver in run A may be due to the above-mentioned difficulty in obtaining constant

TABLE 1

Results of a run upon an unsaturated amalgam

Run A (test run): temperature, $28 \pm 2^\circ$; length of run, 3 hours; weight of silver taken, 0.9894 g.; weight of mercury taken, 2700 g.; atomic per cent of silver taken, 6.81×10^{-2}

SAMPLE NUMBER	WEIGHT OF SILVER	WEIGHT OF AMALGAM	ATOMIC PER CENT OF SILVER $\times 100$	DEVIATION FROM MEAN
	grams	grams		p.p.t.
A-1	0.0838	226.9	6.87	2.9
A-2	0.0725	195.5	6.90	7.3
A-3	0.0750	203.1	6.87	2.9
A-4	0.0703	191.3	6.83	2.9
A-5	0.0614	167.5	6.82	4.4
A-6	0.0627	170.4	6.84	1.5
A-7	0.0672	182.5	6.85	0.0

Average atomic per cent of silver..... 6.85×10^{-2}
 Average deviation from mean..... 3.1 parts per thousand
 Deviation from atomic per cent taken..... 5.8 parts per thousand

TABLE 2

The results of a typical experiment

Run G: temperature, 5.72°C .; length of run, 30 hours; equilibrium approached from high side

SAMPLE NUMBER	WEIGHT OF SILVER	WEIGHT OF MERCURY	ATOMIC PER CENT OF SILVER $\times 100$	DEVIATION FROM MEAN
	grams	grams		p.p.t.
G-1	0.0620	274.1	4.03	0.0
G-2	0.0611	270.0	4.03	0.0
G-3	0.0613	271.5	4.03	0.0
G-4	0.0652	289.0	4.03	0.0
G-5	0.0652	288.5	4.04	2.5
G-6	0.0658	290.1	4.21	45.0 Exclude
G-7	0.0644	285.8	4.01	5.0

Average atomic per cent of silver..... 4.03×10^{-2}
 Average deviation from mean..... 1.3 parts per thousand

weights of the residues. It is not believed that a constant error of this magnitude was present in the other runs.

Table 2 gives the results of a typical experiment. Table 3 summarizes the data. In it are presented the temperatures at which the solubility

determinations were made, the solubility in atomic per cent as measured and as calculated from DeRight's equation, the number of samples taken for analysis, the average deviation from the mean of the samples, and the

TABLE 3
Summary of the data

RUN	TEMPERATURE	SOLUBILITY ATOMIC PER CENT $\times 100$		DEVIATION FROM MEAN	NUMBER OF SAMPLES	TIME
		Measured	From equation			
	$^{\circ}\text{C.}$			<i>p.p.t.</i>		<i>hours</i>
B	19.24	6.52	6.42	7.7	8	8
C	16.12	5.86	5.85	4.1	9	8
D	18.98	6.25	6.37	1.4	8	8
E	12.39	5.19	5.21	1.5	8	11
F	9.71	4.74	4.79	1.3	7	20
G	5.72	4.03	4.21	1.3	6	30

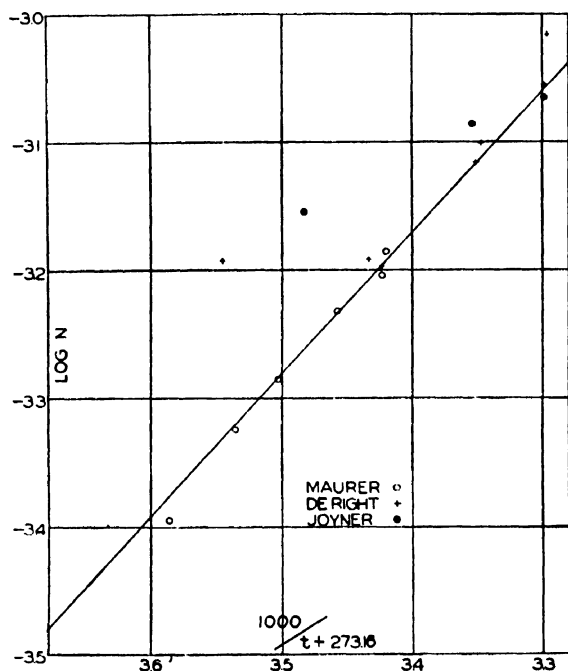


FIG. 2. Plot of the data obtained and also of the data of DeRight and Joyner

time allowed for equilibrium to be reached. In runs D and E equilibrium was approached from the unsaturated side; in all other runs equilibrium was approached from the supersaturated side. One sample in run D and

one sample in run G were excluded because they deviated from the mean by more than four times the average deviation.

DISCUSSION

The results of the present investigation are shown in figure 2 for comparison with the data of DeRight and of Joyner below 30°C. The straight line given by the equation

$$\log N = -\frac{1105.8}{T} + 0.5894$$

is that proposed by DeRight as the best fit for his data from 80° to 10°C. If a large-scale plot of the data of Sunier and Hess, DeRight, and the present data, covering the range 5° to 200°C., is made, a slight deviation from a straight line, as suggested by the present data, is definitely noticeable.

It is felt that the use of a sintered glass filter is an improvement over the use of glass wool and a capillary for filtration as used by DeRight and by Parks and Campanella (working with lanthanum amalgams) (4), in that the conditions of filtration are more reproducible. The use of sintered filters of various pore sizes might shed light upon the question of the influence of the conditions of filtration upon apparent solubility. No support can be found in the present work for the hypothesis of DeRight that below 40°C. silver aggregates of various sizes are present. At least the use of a sintered filter gives sufficiently reproducible conditions to eliminate erratic results.

SUMMARY

1. The solubility of silver in mercury has been determined at six temperatures between 5° and 20°C., confirming the extension of DeRight's equation into this region.

2. A sintered glass filter proved highly satisfactory as a means of separating solid and liquid phases.

The writer wishes to thank Doctor Arthur A. Sunier, who suggested this work and maintained a constant interest in it.

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THE POTENTIALS OF PLATINUM ELECTRODES IN PHOTOGRAPHIC DEVELOPERS¹

A. E. CAMERON

Kodak Research Laboratories, Rochester, New York

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In a recent communication from these Laboratories, R. M. Evans and W. T. Hanson (2) have described the measurement of potentials of blank platinum electrodes immersed in solutions of photographic organic developers and discussed the photographic significance of the potentials so measured. They regarded these potentials as belonging to a possible oxidation-reduction system present, and postulated the existence of a small and essentially constant amount of the oxidized form of the system in equilibrium with sodium sulfite and with the reduced form of the monosulfonate of the developing chemical. Their measurements were made in a vessel exposed to the air, and an investigation of the part which oxygen might play in the production of the potentials was undertaken by the writer in an effort to clarify the precise origin of the observed potentials.

EXPERIMENTAL

Measurements were made in a 250-ml. water-jacketed beaker which was fitted with a glass cap carrying the necessary electrodes, salt bridge, stirrer, etc. Any desired atmosphere could be maintained in this reaction vessel by passing gas in through a porous alundum bubble head. Rapid stirring with a motor-driven glass paddle which entered the reaction vessel through a water seal aided in securing equilibrium conditions.

Readings of the electrode potentials were made with a Leeds and Northrup student type potentiometer with a current galvanometer of medium sensitivity. Readings were, in general, made with a series resistance of 10,000 ohms to avoid or minimize polarization of the electrodes. No criterion of correctness of readings was available, so that agreement of two electrodes within 2 to 3 millivolts was considered satisfactory. Electrodes of virgin platinum foil 1 cm. square were used and were stored in a solution of chromic acid in sulfuric acid between readings. With these electrodes it was found that the potentials were stable and reproducible under stable and reproducible conditions.

¹ Communication No. 654 from the Kodak Research Laboratories.

The values of the pH of the solutions were determined with a glass electrode, using a ballistic galvanometer and one microfarad condenser as an indicator of the potentiometric balance. The electrode was frequently calibrated against the hydrogen electrode in solutions of the same sodium-ion and buffer-ion composition as those in which the potential measurements were made. To make these calibrations the sodium sulfite in the developer solutions was replaced with sodium sulfate. The sodium-ion content of all solutions was maintained at 1.5 *N* by adding anhydrous sodium sulfate, and the buffering ion was 0.2 *N*. The values of pH as recorded are correct to within 0.05 pH unit.

The 3.5 *N* calomel half-cell with the bridge employed is assigned a value of 0.2502 volt against the normal hydrogen electrode at 20°C., and this

TABLE 1

Behavior of the potential as a function of pH for two partial pressures of oxygen
8 g. of elon and 64 g. of sodium sulfite per liter

pH	<i>E</i>	
	21 PER CENT OXYGEN	100 PER CENT OXYGEN
3.60	0.309	0.323
4.45	0.247	0.269
5.43	0.188	0.211
5.85	0.174	0.205
6.45	0.129	0.159
7.13	0.097	0.124
9.05	0.016	0.036
9.10	0.020	0.039
9.30	0.029	0.049
10.10	-0.030	-0.008
10.90	-0.038	-0.012
11.25	-0.028	-0.001
11.43	-0.053	-0.035

value has been used throughout in the calculations of E_H . All measurements were made at 20°C. \pm 0.01°.

The photographic developing agents used were Eastman tested photographic chemicals, and all other chemicals used were of reagent quality. Mixtures of oxygen and nitrogen were prepared from cylinders of the compressed gases and were stored over water. These mixtures were analyzed for oxygen each time the mixture was used, by adsorption in alkaline pyrogallol solution according to the standard gas analysis procedure.

A preliminary investigation with *p*-methylaminophenol (elon) solution in the presence of sodium sulfite at pH = 9 showed that the potentials were dependent upon the partial pressure of oxygen and that the plot of potential against \log_{10} of the percentage of oxygen in the saturating mix-

ture was linear from 1 per cent to 100 per cent. The behavior of the potential as a function of pH was determined for two partial pressures of oxygen, and the data in table 1 are shown graphically in figure 1.

Constancy of behavior with respect to dependence upon the partial pressure of oxygen is indicated in any given range of pH by parallelism of the straight lines for 100 per cent oxygen and 21 per cent oxygen, while a change in this dependence is indicated by a change in the relative spacing of the two lines on the potential axis. It will be noted that a change in

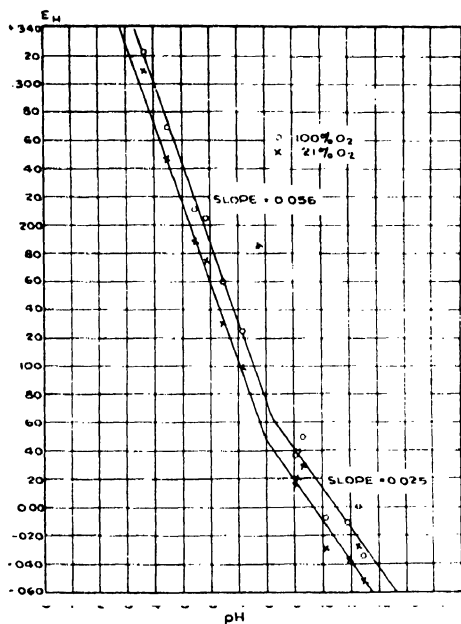


FIG. 1

FIG. 1. Potentials of electrodes in a solution of 8 g. of sodium sulfite per liter, as a function of pH at two different oxygen concentrations.

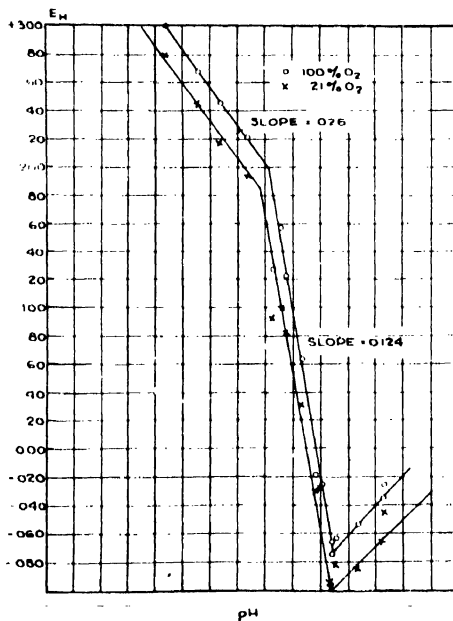


FIG. 2

FIG. 2. The potentials of platinum electrodes in a solution of 5.12 g. of hydroquinone and 64 g. of sodium sulfite per liter, as a function of pH.

the effect of oxygen occurs at $\text{pH} = 8.5$. Similar data for hydroquinone are given in table 2.

It will be noted from the plot of these data in figure 2 that there are three different reaction regions. The readings taken with hydroquinone and with elon at the higher values of pH are not so reliable, however, because of the very rapid reaction of the compounds with oxygen, which makes maintenance of saturation of the solution with oxygen very difficult.

The dependence of the potentials upon the partial pressure of oxygen and upon the concentration of the reducing agent was determined in the

TABLE 2
5.12 g. of hydroquinone and 64 g. of sodium sulfite per liter

pH	E_H 21 PER CENT OXYGEN	E_H 100 PER CENT OXYGEN
4.40	0.280	0.301
5.60	0.246	0.268
6.40	0.218	0.246
7.40	0.195	0.222
8.30	0.093	0.127
8.68	0.100	0.157
8.80	0.083	0.123
9.35	0.031	0.063
9.85	-0.030	-0.019
10.05	-0.045	-0.025
10.40	-0.097	-0.075
10.40	-0.094	-0.066
10.55	-0.081	-0.063
11.35	-0.084	-0.053
12.25	-0.065	-0.035
12.30	-0.044	-0.026

TABLE 3
Dependence of the potentials upon the partial pressure of oxygen and the concentration of the reducing agent
64 g. of sodium sulfite per liter

pH	PER CENT OXYGEN	GRAMS OF ELON PER LITER	E_H
5.85	2.7	0.8	0.180
5.85	21.0	0.8	0.219
5.85	100.0	0.8	0.250
5.85	1.4	8.0	0.128
5.85	21.0	8.0	0.174
5.85	100.0	8.0	0.205
5.85	1.4	16.0	0.108
5.85	21.0	16.0	0.159
5.85	100.0	16.0	0.188
9.30	1.2	0.8	0.033
9.30	21.0	0.8	0.071
9.30	100.0	0.8	0.095
9.30	1.2	4.0	0.005
9.30	21.0	4.0	0.043
9.30	100.0	4.0	0.065
9.30	1.3	8.0	-0.005
9.30	21.0	8.0	0.029
9.30	100.0	8.0	0.049

TABLE 5

Dependence of the potentials upon the concentration of sodium sulfite

MOLES OF SODIUM SULFITE PER MOLE OF ELON	E_H	
	21 PER CENT OXYGEN	100 PER CENT OXYGEN
8 g. of elon per liter; pH = 9.05		
0.35	0.038	0.056
0.35	0.033	0.051
0.70	0.043	0.059
2.10	0.033	0.050
3.52	0.033	0.050
4.57	0.039	0.058
4.57	0.027	0.046
5.63	0.015	0.034
5.63	0.020	0.040
5.63	0.022	0.042
11.25	0.009	0.035
11.25	0.015	0.034
11.25	0.017	0.037
8 g. of hydroquinone per liter; pH = 9.40		
0.87	-0.005	0.016
1.75	-0.017	0.003
1.75	-0.009	0.010
3.49	-0.013	0.011
3.49		0.007
7.00	-0.020	0.003
7.00		0.000

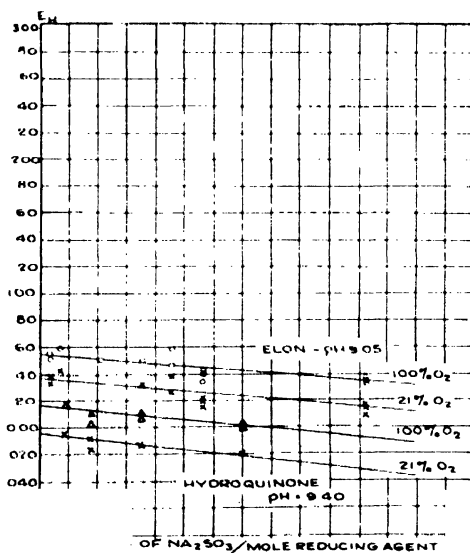


FIG. 5. Electrode potentials of solutions containing 8 g. of elon or 8 g. of hydroquinone per liter, as a function of concentration of sodium sulfite at constant pH.

ranges of pH in which the potential-pH relationship indicated constancy of behavior. The data are given in table 3 and are shown graphically in figures 3 and 4. Because of the extremely rapid reaction with oxygen at high pH values, the range above pH = 10 was not investigated in this manner.

The dependence of the potentials upon the concentration of sodium sulfite was investigated for both compounds. The results are tabulated in table 5 and plotted in figure 5.

DISCUSSION

The dependence of the potentials upon the partial pressure of oxygen eliminates the possibility that the observed potentials are due to a thermodynamically reversible oxidation-reduction system, the oxidized form of which is present in small and essentially constant concentration. Furthermore, the potential-pH relationships for the two compounds investigated show no parallelism in behavior to the oxidation-reduction potentials of the systems. Fieser (3) has determined the oxidation-reduction potential of *p*-methylaminophenol from pH = 0 to pH = 8 by a discontinuous titration method, and the writer has extended these measurements to pH = 13.5. The oxidation-reduction potential of this compound as a function of pH shows the following behavior:

pH range	Slope
0 - 4.0	0.058
4.0 - 5.75	0.087
5.75 - 10.40	0.058
10.40 - 13.50	0.029

The slopes as given are those which are theoretical for 20°C., and the experimental points fell very precisely upon them. The slopes found for the electrode potentials for elon in the presence of sodium sulfite, referring to figure 1, are as follows:

pH range	Slope
3.5 - 8.3	0.056
8.3 - 11.5	0.025

The numerical slopes are in rough agreement with those of an oxidation-reduction system, but the 0.087 slope, which should appear between pH = 4 and pH = 5.75, is absent. Furthermore, there is a discrepancy of two pH units in the two cases between the change from the 0.058 slope to what approximates an 0.029 slope in the case of the potentials in the presence of sodium sulfite.

In the case of the system hydroquinone-quinone, the oxidation-reduction potential has the slope of 0.058 from pH = 0 until the pK of the first acid ionization is reached. The ionization constant of the first acid

ionization of hydroquinone at 18°C. is given by Von Euler and Brunius (1) as 1.33×10^{-10} , and the pK is 9.98. Sheppard (5) gives the first ionization constant as 1.75×10^{-10} at 25°C., and the corresponding pK is 9.75. Therefore, in the case of the hydroquinone-quinone system there should be a change from a slope of 0.058 to 0.029 at about pH = 9.90, and no change in slope before this. The potentials measured in the presence of sodium sulfite show none of this behavior. From pH = 4 to pH = 8 the slope is 0.026 instead of 0.058, and from pH = 8 to pH = 10.3 it is 0.124. Above a pH of 10.3 the slope seems to reverse its sign, although measure-

TABLE 6

The slopes of the dependence of potential upon the partial pressure of oxygen and the concentration of the reducing agent

REDUCING AGENT	pH RANGE	SLOPE OF E_H -pH	SLOPE OF E_H -[Red]	SLOPE OF E_H -PER CENT OXYGEN
Elon	3.5- 8.3	0.056	0.048	0.045
			0.045	0.043
			Av. = 0.046	0.043
			Av. = 0.043	
	8.3-11.5	0.025	0.044	0.033
			0.042	0.031
			Av. = 0.043	0.029
				0.032
			Av. = 0.031	
	4.0- 8.0	0.026	0.008	0.031
0.010			0.032	
Av. = 0.009			0.034	
Av. = 0.032				
Hydroquinone	8.0-10.3	0.124	0.041	0.037
			0.044	0.040
			Av. = 0.042	0.041
			Av. = 0.039	

ments in this region should not be too heavily relied upon because of the rapid reaction taking place between oxygen and hydroquinone.

Potentials measured in an atmosphere of pure nitrogen are much lower than those recorded above and are unpoised, as would be expected in a solution containing only one component of an oxidation-reduction system. Readings agreeing roughly with those obtained in pure nitrogen can be secured from electrodes located at the bottom of a beaker of unstirred solution exposed to air. As the oxygen present in the solution is used up, the potentials fall and become less well poised.

The slopes of the dependence of potential upon the partial pressure of oxygen and the concentration of the reducing agent are summarized in table 6. It will be observed that in no case is the slope of the dependence of potential upon concentration of reduced form that which would be expected for a two-electron oxidation-reduction system. The general expression for such a system at constant pH is the following:

$$E_H = E_0 - 0.029 \log_{10} \frac{[\text{Red}]}{[\text{Ox}]}$$

from which it is apparent that a tenfold change in the concentration of the reduced form, the concentration of oxidized form being held constant, would cause a decrease in the observed potential of 0.029 volt.

The effect of sodium sulfite upon the potentials of these two systems is shown in figure 5. It will be noted that the effect of sulfite upon the potentials is a linear function of the sulfite concentration instead of being a

TABLE 7
Values of *a* and *b*

REDUCING AGENT	pH	<i>a</i>	<i>b</i>
Hydroquinone	3.5 8.3	3	3
	8.3 11.5	3	2
	4.0 8.0	1	2
	8.0 10.3	3	3

linear function of the logarithm of this concentration. The sulfite removes the oxidized form as the monosulfonate, and destroys the oxidation-reduction system which would otherwise be present. Beyond this, no definite function can be ascribed to the sulfite as far as the determination of these potentials is concerned.

If oxygen is regarded as the basic unit involved in the electrode reaction, involving an electron transfer of four for each molecule of oxygen, the following expression can be set up for the electrode potentials at constant pH and constant sulfite concentration:

$$E_H = E_0 - 0.015 \log_{10} \frac{[\text{Red}]^a}{[\text{O}]^{1b}}$$

The values of the exponents *a* and *b* can be determined from the slopes of the potential-concentration relationships given in table 6. In the case of elon, the observed slopes seem to be definite multiples of 0.015, but in the case of hydroquinone this is not so well defined. The interpretation of these expressions in terms of an electrode reaction is not possible at

the present time. It must be noted, however, that the reducing agent and molecular oxygen occur on *opposite* sides of the equilibrium, since an increase in concentration of the reducing agent shifts the potentials to lower values and an increase in concentration of molecular oxygen shifts it toward higher values.

A discussion of the significance of these potentials for photographic theory or practice lies beyond the intended scope of this paper. It may be indicated in passing, however, that measurements made in developer solutions which have been in contact with photographic emulsion may be in considerable error. Colloidal silver, an autoxidation catalyst, causes a shift of the potentials to lower values without changing the slope of the potential-oxygen concentration relationship. Silver ion causes the blank platinum electrode potentials to become independent of the oxygen concentration. The electrodes then behave like silver electrodes. This effect has been described by Kolthoff and Wang (4) for silver-ion concentrations above 0.01 *M*. Even very low concentrations of silver ion appear to cause this effect.

It appears to be possible to measure potentials which show similar behavior in any system, organic or inorganic, which does not give rise to a reversible oxidation-reduction system upon oxidation by molecular oxygen. Examples of these are benzoic acid in strongly alkaline solution and sodium sulfite.

SUMMARY

1. The potentials of blank platinum electrodes in photographic developer solutions are found to be functions of the oxygen concentration as well as of the concentration of the reducing agent.

2. The reducing agent and molecular oxygen take part in the electrode reaction upon opposite sides of the equilibrium.

3. The most apparent effect of sodium sulfite is to destroy any reversible oxidation-reduction system which might otherwise mask the "oxygen" electrode potential.

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THE POSTPRECIPITATION OF ZINC SULFIDE WITH BISMUTH SULFIDE¹

I. M. KOLTHOFF AND FRANK S. GRIFFITH

School of Chemistry, University of Minnesota, Minneapolis, Minnesota

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In previous investigations carried out in this laboratory it was shown that the induced precipitation of zinc sulfide from acid medium by copper sulfide (7) and mercuric sulfide (5) actually is a postprecipitation. The rate of precipitation of zinc sulfide from acid medium is small, but is greatly enhanced at the interphase of the copper or mercuric sulfides. Conclusive evidence was given that the promoting effect of these sulfides upon the postprecipitation of zinc sulfide is to be attributed to the presence of an adsorbed layer of hydrogen sulfide at the interphase, the acid being, partially at least, ionized in the adsorbed state. The results of Caldwell and Moyer (3) substantiate the views developed in previous papers (6). In the postprecipitation of zinc sulfide induced by copper sulfide the former precipitates as a separate phase and can be readily extracted from the mixed precipitate with 3 *N* hydrochloric acid. The zinc sulfide postprecipitated by mercuric sulfide forms to a limited extent mixed crystals with the latter; this explains why the zinc is not easily extracted from the mixed precipitate with 3 *N* hydrochloric acid. From our own work and from the extensive study by Böttger and Ahrens (1) it may be concluded that cadmium sulfide is also postprecipitated with mercuric sulfide, and that the mixed precipitates of the two consist of mixed crystals.

In the present study the effect of bismuth sulfide upon the precipitation of zinc sulfide was investigated. Bismuth sulfide was chosen not only because it has a different crystal structure from zinc sulfide (in this respect it is comparable with copper sulfide), but also because it is of a different formula type. Zinc sulfide crystallizes either in the cubic or in the hexagonal system, whereas bismuth sulfide crystals belong to the orthorhombic system.

EXPERIMENTAL

Materials used

All chemicals used were c. p. products. The stock solutions of bismuth chloride were 1 normal with respect to hydrochloric acid in order to pre-

¹ This article is based on a thesis submitted by Frank S. Griffith to the Graduate School of the University of Minnesota in partial fulfillment of the requirements for the degree of Doctor of Philosophy, June, 1937.

vent the separation of bismuth oxychloride. After mixing with the zinc and other solutions the acid concentration was reduced and a white precipitate of bismuth oxychloride was formed, the latter being transformed to bismuth sulfide when the solution was saturated with hydrogen sulfide. It was also desirable to investigate the effect of bismuth sulfide separated from clear solutions. In such cases the stock solution of bismuth chloride was 0.4 *N* in hydrochloric acid and contained 50 g. of tartaric acid per liter. No precipitate separated from such a solution upon dilution.

Analytical

After the treatment with hydrogen sulfide the zinc was determined in the filtrate by titration with potassium ferrocyanide, using diphenylamine as indicator (8).

Reproducibility of experiments

In the early work great differences were found between results of apparently identical experiments; for example, 68 per cent and 46 per cent of the zinc were found precipitated in two experiments supposedly identical, but run on different days. After a systematic search it was found that, in general, the amount of postprecipitated zinc sulfide decreased with depletion of the Kipp generator in which the hydrogen sulfide was produced by the interaction of stick iron sulfide and commercial hydrochloric acid. The iron sulfide contains free iron which leads to a dilution of the hydrogen sulfide with hydrogen. The gas generated was tested for hydrogen by removing the hydrogen sulfide by absorption in sodium hydroxide. The amount of hydrogen present was found to vary between 2 and 18 per cent, depending upon the use and age of the generator. With fresh 3 *N* hydrochloric acid in the generator, 1.6 per cent hydrogen was found when the gas was withdrawn at a rapid rate; when the rate was decreased to 75 bubbles (about 20 ml.) per minute the percentage of hydrogen increased to 10 per cent. When the generator was allowed to stand unused for a few hours, the percentage of hydrogen in the gas at the start of the next discharge was found to be unusually high (18 to 20 per cent).

In order to keep the hydrogen sulfide pressure constant it would be preferable to use gas from a tank. As the latter was not available the error due to varying composition of the gas was mainly eliminated by running standard comparison experiments or identical experiments in series with the particular system investigated.

Experimental procedure

In general the same method of precipitation was used as described in the paper of Kolthoff and Moltzau (5). The precipitate was removed by filtration and washed eight to ten times with 0.1 *N* hydrochloric acid

saturated with hydrogen sulfide. The solubility of the zinc sulfide in this wash solution was low. In some cases the precipitate was subjected to twenty-five more washings after the ten usual washings; it was found that only 1 per cent of the total zinc was removed by the twenty-five extra washings when the total amount of zinc in the system was about 1.25 millimoles.

TABLE 1

Effect of concentration of acid and time of shaking upon postprecipitation of zinc sulfide at 25°C.

CONCENTRATION OF HCl BEFORE PRECIPITATION OF ZINC	TIME OF SHAKING	ZINC PRECIPITATED*
<i>N</i>	<i>minutes</i>	<i>per cent</i>
0.15	5	30
0.15	15	75
0.15	60	90
0.15 (blank)†	60	2
0.20	5	0.5
0.20	15	31
0.20	60	82
0.20 (blank)†	0	0.5
0.25	5	0.0
0.25	15	0.5 3
0.25	60	32
0.30	60	2
0.30	180	7

* The average value of two to four experiments is given.

† The blanks contained 25 ml. of water, instead of 25 ml. of the bismuth solution.

RESULTS

Effect of acidity upon postprecipitation

In the following experiments 25 ml. of 0.05 *M* bismuth chloride solution, which was normal with respect to hydrochloric acid, was mixed with 25 ml. of 0.05 *M* zinc chloride; a measured volume of 5.9 *N* sodium hydroxide was added to obtain the acid concentration (after precipitation of the bismuth as sulfide) indicated in table 1. The total volume was made up to 55 ml. The solutions were shaken continuously while hydrogen sulfide was passed through the flasks at a constant rate.

From the results, particularly in 0.25 *N* hydrochloric acid, it follows conclusively that we are dealing again with a postprecipitation of the zinc sulfide. From the analytical viewpoint it is of interest to notice that a quantitative separation of bismuth and zinc is obtained when the initial

hydrochloric acid concentration is 0.3 *N* and the filtration is made a few minutes after the precipitation of the bismuth sulfide.

In the above experiments part of the bismuth was precipitated as oxychloride before hydrogen sulfide was passed through. In order to keep all of the bismuth in solution, experiments were carried out in the presence of tartaric acid. A mixture was prepared from 25 ml. of 0.05 *M* bismuth chloride which was 0.4 *N* in hydrochloric acid and 0.3 *M* in tartaric acid, 25 ml. of 0.05 *M* zinc chloride which was 0.1 *N* in hydrochloric acid, and 1 ml. of 5.15 *N* sodium hydroxide. The final hydrochloric acid concentration (after precipitation of the bismuth) was 0.2 *N*. The air was removed by passing a rapid stream of hydrogen sulfide through the flask for half a minute; this was continued for 2 minutes after the shaker was started, then decreased for 3 minutes to a stream which just broke into bubbles as it passed through the wash bottle, and finally decreased to a rate of about 150 bubbles per minute for the remainder of the precipitation period. In these experiments pure hydrogen sulfide prepared by heating a magnesium hydrosulfide solution and stored in a gas holder was used. Under identical conditions the experiments were well reproducible. The results are given in table 2.

TABLE 2

Postprecipitation of zinc sulfide from 0.2 N hydrochloric acid solutions containing tartaric acid at 25°C.

Time of shaking in minutes.	18	33	48	63
Zinc precipitated in per cent.	3	20	47	69

Again it is seen that the amount of zinc sulfide precipitated increases with the time of contact with bismuth sulfide when the solution is saturated with hydrogen sulfide. A comparison of the results with those in table 1 at the same acidity reveals that tartaric acid inhibits the postprecipitation. As the experiments in the two tables were carried out under different conditions of hydrogen sulfide treatment, a new set was made under identical conditions, using a shaking period of 30 minutes and a hydrochloric acid concentration of 0.2 *N*. In the absence of tartaric acid 45 per cent of the zinc was found precipitated; in the presence of tartaric acid 18 per cent. These experiments show conclusively the inhibiting effect of tartaric acid upon the postprecipitation of zinc sulfide on bismuth sulfide. In the absence of tartaric acid the greatest part of the bismuth sulfide is obtained by transformation of the precipitated bismuth oxychloride into sulfide, whereas in the presence of tartaric acid it is obtained from a clear solution. Apparently the structure of the sulfide formed in the absence of tartaric acid is such that it has a greater promoting effect upon the postprecipitation of zinc sulfide than when formed from

tartaric acid-containing solutions. Addition of tartaric acid to 0.05 *M* zinc chloride which was 0.1 *N* with hydrochloric acid did not appreciably affect the rate of precipitation when no promoting sulfide was present. From this it is inferred that the inhibiting effect of the tartaric acid is, for the most part, not due to complex formation with zinc.

Incidentally, it may be mentioned that the rate of postprecipitation decreases with increasing sodium chloride content of the solution. The experiments reported in table 2 were repeated, but with the addition of 2.5 g. of sodium chloride to the mixture. After half an hour of shaking 1 per cent of the zinc was precipitated, whereas 18 per cent was found precipitated when no sodium chloride was added. A similar inhibiting effect of sodium chloride was found by Kolthoff and Pearson (7) in the postprecipitation of zinc sulfide by copper sulfide.

Comparison of the effectiveness of the sulfides of copper, bismuth, mercury, and zinc on the precipitation of zinc sulfide

The experiments were carried out with 1.25 millimoles of the promoting sulfide and 1.25 millimoles of zinc chloride, the hydrochloric acid concentration being 0.2 *N* after precipitation of the promoting sulfide and the

TABLE 3

Comparison of promoting effect of sulfides of copper, bismuth, mercury, and zinc on precipitation of zinc sulfide

Promoting sulfide	Bi	Cu	Hg	Zn
Zinc precipitated in per cent	45	36	85	83
Sodium chloride present in grams	1.0	1.4	1.2	0.30

total volume 55 ml. In all cases the hydrogen sulfide was passed through the mixture of the metal sulfide and zinc salt for 30 minutes. The zinc sulfide used as promoting agent was prepared by passing hydrogen sulfide through a slightly acid (0.002 *N*) solution of 0.05 *M* zinc chloride; the other promoting sulfides were precipitated in the presence of the zinc solution. The results are given in table 3.

The results are not strictly comparable, as the sodium chloride contents of the various solutions were not identical. Still, it may be concluded that mercuric and zinc sulfides have about the same promoting effect on the precipitation of zinc sulfide, the effect of bismuth and copper being less. Such a result is probably explained by the fact that mercuric sulfide and zinc sulfide crystallize in the same system and form mixed crystals (5), whereas bismuth sulfide and copper sulfide crystallize in different systems. The induction period in the postprecipitation of zinc with mercuric sulfide may, therefore, be expected to be materially shorter than with the other sulfides. A quantitative comparison of the figures in table 3 is not per-

missible, as the promoting effect of a certain sulfide depends upon the conditions of precipitation. This is particularly true of the zinc sulfide. In the above case it was precipitated from very dilute acid solution and was very finely divided. If prepared from stronger acid medium it would be coarser and would have less inducing effect upon the precipitation of zinc from solution. This may explain the result of Glixelli (4), who found copper sulfide to be a more efficient promotor of the precipitation of zinc sulfide than the latter; he describes the zinc sulfide used as being fresh, but does not state the conditions under which it was precipitated.

Effect of aging of bismuth sulfide

In the following experiments a mixture of 25 ml. of 0.05 *M* bismuth chloride solution and enough 5.15 *N* sodium hydroxide to make the acid concentration 0.206 *N* after the precipitation of bismuth was treated with hydrogen sulfide and shaken, with a slow stream of hydrogen sulfide passing through it, until the sulfide had aged for a given period of time. Then 25 ml. of 0.05 *M* zinc chloride which was 0.1 *N* in hydrochloric acid was added, and the flask shaken while a slow stream of hydrogen sulfide passed through for 30 minutes. Acid had to be added to the zinc solution in order to prevent the precipitation of zinc sulfide, as the solution was pipetted into the flask full of hydrogen sulfide. In order to get results comparable with the effect of a fresh precipitate, a mixture of the bismuth-sodium hydroxide-zinc solution was treated with hydrogen sulfide for 30 minutes in exactly the same way. The reproducibility of the experiments was poor, but all of the twenty experiments showed the same trend.

The bismuth sulfide aged for 10 minutes caused the precipitation of 20 per cent less zinc than the fresh precipitate, the 15- to 20-minutes old precipitate 24 per cent less, the 60-minutes old precipitate 25 per cent less, but a 41-hours old precipitate 10 per cent *more*. A precipitate aged for a day had about the same promoting effect upon the precipitation of zinc sulfide as fresh bismuth sulfide. It was thought that the separation of bismuth oxychloride before the passage of hydrogen sulfide might account for the unexpected and badly reproducible results. For this reason a great number of experiments was run in which the precipitation of the oxychloride was prevented by addition of tartaric acid.

The final composition of the mixture was about the same as that used in the experiments of table 2, the period of precipitation of zinc being again 30 minutes. In all cases blanks were run with the entire mixture (fresh bismuth sulfide) in series with the experiments with aged bismuth sulfide.

In some instances the bismuth sulfide was aged at 85°-95°C.; the temperature dropped during the aging, as in general no further heat was supplied. After the period of aging the sample was cooled as quickly as possible, and resaturated with hydrogen sulfide, then the zinc chloride

was added and the sample further shaken in a slow stream of hydrogen sulfide for 30 minutes. The results are given in table 4.

In the presence of tartaric acid the bismuth sulfide, even upon short periods of aging, becomes more effective in the promotion of the precipitation of zinc sulfide than a fresh product. The effectiveness increases with the age of the bismuth sulfide, until after a relatively long period a maximum is reached. Thus it is seen from table 4 that bismuth sulfide aged at room temperature for 42 hours caused the precipitation of 63 per cent more zinc than the fresh precipitate; after aging for 6 months it had about the same promoting effect as a fresh precipitate. Similar results are found when the bismuth sulfide is aged at 80°-90°C. The 10-minutes old product caused 69 per cent more of the zinc to precipitate than the fresh prod-

TABLE 4

Effect of aging of bismuth sulfide upon its promoting effect on precipitation of zinc sulfide

TEMPERATURE OF AGING °C.	AGE OF BISMUTH SULFIDE	PER CENT ZINC PRECIPITATED* AFTER 30 MINUTES		DIFFERENCE BETWEEN (a) AND (b)
		Aged Bi ₂ S ₃ (a)	Fresh Bi ₂ S ₃ (b)	
25	10 minutes	31	18	+13
25	1 hour	45	18	+27
25	42 hours	83	20	+63
25	6 months	15	16	-1
85-95	10 minutes	69	18	+51
80	4 days	10	16	-6

* Average values of three to six experiments.

uct; after aging for 4 days at 80°C. the sulfide became less effective than the fresh precipitate.

No study has been made of the structural changes taking place during the short and long periods of aging of bismuth sulfide at various temperatures. From the data of table 4 it may be expected that such a study will yield interesting results.

It may be mentioned that it is immaterial whether the bismuth sulfide is shaken or allowed to stand quietly during the aging period. Entrance of air during the aging decreases the effectiveness of the bismuth sulfide somewhat; probably some sulfur formed by oxidation of hydrogen sulfide separates on the surface of the sulfide.

Postprecipitation at higher temperatures

Experiments were carried out with a mixture of bismuth and zinc chlorides of the same composition as that in the experiments reported in table

1. The hydrochloric acid concentration after the precipitation of bismuth was 0.2 *N*, and the time of shaking 60 minutes. One set of experiments was carried out at 50°C., another set at 25°C. In the former 32 per cent of the zinc was found precipitated, in the latter 80 per cent.

Extractibility of the zinc from the mixed sulfides

Precipitates obtained under the same conditions as those of table 2 after a shaking period of 60 minutes, and washing, were shaken for 1 hour with 75 ml. of 3 *N* hydrochloric acid at room temperature, the liquid decanted through a filter, and the residue shaken for 3 more hours with a fresh portion of the acid. The filtrates were evaporated to small volumes and diluted, and the bismuth which had dissolved was reprecipitated with hydrogen sulfide. The zinc was determined in the filtrates. The following results were obtained: per cent of zinc in the original filtrate, 30.0; in the first extraction, 68.1; in the second, 2.5; total, 100.6 per cent. It appears that the zinc is fairly easily extracted from the precipitate. It may be objected (Balarew (2)) that the easy extractibility is due to air oxidation of the zinc sulfide and to solution of some of the bismuth. In order to eliminate this objection experiments were carried out with a bismuth-zinc solution (final acidity 0.22 *N*, further composition as in table 1) treated for 30 minutes with hydrogen sulfide. The mixture was transferred to a volumetric flask of 100 ml. and made up to volume with 0.2 *N* hydrochloric acid saturated with hydrogen sulfide. After mixing and allowing to settle, 50 ml. of the clear solution was pipetted out and analyzed for zinc. The remainder was filtered, washed with 0.2 *N* hydrochloric acid saturated with hydrogen sulfide (called "remainder"), and then the precipitate with paper dropped into 50 ml. of 2 *N* hydrochloric acid saturated with hydrogen sulfide. The mixture was shaken for 40 minutes while hydrogen sulfide was passed through, was filtered (extraction 1), and the extraction was repeated (extraction 2). No bismuth dissolved during this extraction process. The following results were obtained: per cent of zinc in 50 ml. pipetted out, 12.1; in remainder, 20.4; in extraction 1, 69.0; in extraction 2, 0.2; total, 101.7 per cent.

Evidently, some of the zinc is already extracted by 0.2 *N* hydrochloric acid saturated with hydrogen sulfide, indicating that the zinc sulfide is very finely divided and hardly aged. Well-aged zinc sulfide is insoluble in 0.2 *N* hydrochloric acid saturated with hydrogen sulfide (Kolthoff and Moltzau (5)). Furthermore, it is seen that the zinc is easily extracted with 2 *N* hydrochloric acid under conditions which preclude oxidation of the zinc sulfide or solution of any of the bismuth. The ready extractibility contrasts markedly with the extractibility of zinc sulfide postprecipitated with mercuric sulfide (5). In the latter case the zinc sulfide forms a solid solution with the mercuric sulfide, whereas mixed-crystal formation does not occur between bismuth sulfide and zinc sulfide.

Kolthoff and Pearson (7) found that zinc sulfide postprecipitated with copper sulfide can be easily extracted from the mixed precipitate. Balarew (2) attributed this ready extractibility to air oxidation of the zinc sulfide. Some of Kolthoff and Pearson's experiments were repeated under the above extraction conditions precluding air oxidation. Again it was found that the zinc was easily extracted, contrary to Balarew's statements.

SUMMARY

1. Zinc sulfide is postprecipitated with bismuth sulfide.
2. Zinc can be separated quantitatively from bismuth when the hydrochloric acid concentration after precipitation of bismuth is at least 0.3 *N* and filtration is made within a few minutes after the bismuth has separated.
3. The rate of postprecipitation of zinc with bismuth sulfide is small during the early periods of shaking and becomes greater with longer periods of contact. In this respect the effect of bismuth sulfide is comparable to that of cupric sulfide, but in contrast to that of mercuric sulfide. In the latter case the rapid initial rate of postprecipitation is attributed to the similarity of the lattices of zinc sulfide and mercuric sulfide, which is responsible for the reduction of the induction period in the precipitation of zinc sulfide.
4. Mercuric and zinc sulfides are more effective in the postprecipitation of zinc sulfide than bismuth and copper sulfides.
5. Bismuth sulfide aged at room temperature or higher temperatures under specified conditions becomes markedly more effective in the postprecipitation of zinc. After long periods of aging it becomes less effective. Copper sulfide behaves in a similar way, but mercuric sulfide becomes less effective on aging.
6. The zinc can be readily extracted with 2 *N* hydrochloric acid from a mixed sulfide with bismuth or copper, but not from a mixed sulfide with mercury. In the latter case part of the zinc is incorporated in the precipitate as mixed crystals.
7. Addition of sodium chloride to the solution inhibits the rate of postprecipitation of zinc sulfide with bismuth (and copper) sulfide.

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A PRELIMINARY STUDY OF THE POSTPRECIPITATION OF NICKEL SULFIDE WITH COPPER, MERCURIC, AND ZINC SULFIDES¹

I. M. KOLTHOFF AND FRANK S. GRIFFITH

School of Chemistry, University of Minnesota, Minneapolis, Minnesota

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Baubigny (1) stated in 1882 that nickel sulfide is very slow to separate from slightly acid (0.01 *N* hydrochloric acid) solutions. The solid, however, rapidly changes in some manner to yield products which are much less soluble in 2 *N* hydrochloric acid than would be expected from its small rate of precipitation in dilute acid (3, 7, 6). The solubility of precipitated nickel sulfide decreases markedly on standing in contact with acid solution; in pure water the effect is less. Higher temperatures seem to hasten the transition. Thiel and Gessner (6) postulated the existence of different "modifications" of nickel sulfide, roughly designated as the α -, β -, and γ -forms, corresponding to more or less definite solubilities in hydrochloric acid of a given strength. They advanced the belief that the different preparations differed in the extent of polymerization, and that differences in solubility were to be attributed to this condition. Although this may be true to a certain extent, differences in crystal structure of the different "modifications" may have to be considered. Recently Levi and Boroni (4) found that nickel sulfide prepared from dilute sulfuric acid medium is identical with millerite, but that the product prepared from acetic acid solutions has a different crystal structure.

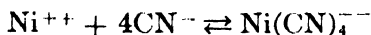
Since the solubility of nickel sulfide decreases considerably with increasing age, it was expected that other insoluble sulfides might induce the precipitation of nickel sulfide at acidities at which the latter is extremely slow to separate in the absence of promoting sulfides. For this reason a preliminary study was made of the postprecipitation of nickel sulfide with the sulfides of copper, mercury, and zinc, respectively.

EXPERIMENTAL

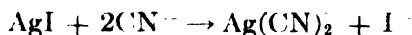
All of the chemicals used were of c. p. quality. The nickel left in the filtrate after the postprecipitation experiments was determined gravimetrically.

¹ This article is based on a thesis submitted by Frank S. Griffith to the Graduate School of the University of Minnesota in partial fulfillment of the requirements for the degree of Doctor of Philosophy, June, 1937.

cally with dimethylglyoxime or, more rapidly, volumetrically by the cyanide method (5). In the latter method the nickel is transformed to the complex cyanide ion



and the end point is indicated by the disappearance of the turbidity of suspended silver iodide:



The location of the end point depends upon the concentrations of iodide and ammonia present. Accurate results were obtained by the following procedure: The nickel solution is diluted to 50–70 ml., 5 ml. of 6 *N* ammonia solution, 1 g. of ammonium sulfate, and 1 ml. of 25 per cent potassium iodide solution are added, and the mixture is titrated with standard potassium cyanide solution until the green-blue color fades. Three or four drops of standard silver nitrate are added and the titration with cyanide continued until the solution becomes clear. A correction is applied for the amount of silver added. The turbidity is best seen if the flask containing the solution is placed on a black underground with a black background behind the flask and a strong light coming from the side. Under the best lighting conditions the end point can be detected with an accuracy of 0.04 ml. of 0.02 *M* cyanide (= 0.01 mg. of nickel) in a total volume of 50 ml.

The ammonium sulfate is added to prevent the precipitation of nickel cyanide during the course of the titration. If such a precipitate forms, it is very slow to redissolve upon further addition of cyanide, thus spoiling the titration. Tartrate and citrate (2) are more effective than ammonium sulfate in preventing the precipitation of nickel cyanide. With the concentrations used in this work only in a few cases did any turbidity result from the separation of nickel cyanide.

The following standard solutions were used: (1) 0.1034 *M* silver nitrate (calculated from the weight of silver nitrate used, 0.1035 *M*; from titration against pure potassium thiocyanate, 0.1033 *M*). (2) 0.1370 *M* potassium cyanide. Twenty grams of potassium cyanide and 40 ml. of 6 *N* sodium hydroxide were diluted to a volume of 2 liters. The solution was standardized against silver nitrate by the Liebig-Dénigès method. (3) 0.05120 *M* nickel sulfate. By precipitation with dimethylglyoxime a molarity of 0.05122 was found; by the volumetric procedure described above a molarity of 0.05118.

If desirable, more dilute solutions were prepared from the standard solutions. In the titration of 25 ml. of the 0.05 *M* nickel solution by the recommended procedure the average deviation found was 0.0 per cent (six determinations; error deviated between + 0.05 and – 0.05 per cent; in the titration of 10 ml. of the nickel solution the average error was 0.13

per cent (varying between 0 and 0.3 per cent). Even very dilute nickel solutions (50 ml. of 0.000512 *M* solution = 1.5 mg. of nickel) could be titrated with an accuracy of 1 per cent. Small amounts of zinc (0.5 millimole) did not interfere with the titration.

TABLE 1

Postprecipitation of nickel sulfide with cupric, mercuric, and zinc sulfides, respectively (at 25°C.)

SET*	AMOUNT OF PRO- MOTING METAL SULFIDE	CONCEN- TRATION OF HCl	TIME OF SHAKING	NICKEL PRECIPITATED IN PER CENT IN THE PRESENCE OF			
				CuS	HgS	ZnS	Blank
	millimoles	<i>N</i>		per cent	per cent	per cent	per cent
1	0.2	0.004	3 hours	3.2	6.0	1.9	0.5
1	0.2	0.004	52 hours	31	56	77.0	23.5
1	0.2	0.004	96 hours	74	86		85.5
2	0.5	0.01	3 hours	0	0	0	0
2	0.5	0.01	12 hours	3.0	3.5	3.0	0
2	0.5	0.01	24 hours	6.5	36	33.0	0
2	0.5	0.01	36 hours	13.5	54	55	0
2	0.5	0.01	60 hours	37.0	82	88	0
3	0.5	0.02	23 hours	0.5	4.0	1.0	0
3	0.5	0.02	59 hours	2.0	46	4.5	0
3	0.5	0.02	81 hours	3.0	69	9.5	0
4	0.5	0.05	2 days	1.4	1.3	0	0
4	0.5	0.05	5 days	6.0	11	0	0
4	0.5	0.05	7 days	16	13	0	0

* Set 1: 100 ml. of 0.05 *M* nickel chloride + 4 ml. of 0.05 *M* cupric, or mercuric, or zinc chloride. Acid concentration after precipitation of promoting sulfide (0.2 millimole) was 0.004 *N*.

Set 2: 100 ml. of 0.05 *M* nickel chloride + 10 ml. of 0.05 *M* cupric, or mercuric, or zinc chloride. Acid concentration after precipitation of promoting sulfide (0.5 millimole) was 0.01 *N*.

Set 3: As set 2, but with 1 ml. of 1.21 *N* hydrochloric acid in addition.

Set 4: As set 2, but with 1.9 ml. of 2.42 *N* hydrochloric acid in addition.

Postprecipitation of nickel sulfide with other sulfides

Nickel sulfide is precipitated very slowly from acid medium. When a 0.04 *M* nickel chloride solution was kept in an atmosphere of hydrogen sulfide a first separation was noticed after 21 hours in 0.005 *N* hydrochloric acid, after 66 hours in 0.01 *N* acid, and none at all even after 20 days in 0.02 *N* acid. With 0.01 *M* nickel chloride solution a first separation of sulfide was noticed after 26 to 28 hours in 0.005 *N* acid, and after 5 days in 0.01 *N* acid.

The results of the postprecipitation experiments are combined in table 1.

Performance of experiments

The 250-ml. Erlenmeyer flasks containing the solutions were placed on a rotary shaker, and hydrogen sulfide was passed through continuously. From time to time the shaker was stopped, the precipitate allowed to settle, and 10 ml. of the liquid pipetted off for nickel analysis. The sample taken for analysis was filtered through a paper which had been previously washed with 0.02 *N* hydrochloric acid, the filter was washed with water, and the filtrate was analyzed for nickel by the cyanide method. Washing the filter with dilute acid appeared necessary, else a slight precipitation of nickel sulfide from the supersaturated solution would occur.

The acid concentration given in table 1 corresponds to that in the solution after precipitation of the more insoluble promoting sulfide. The experiments whose results are given in the column headed "blank" had no inducing sulfide present but were of the same volume and contained the same amounts of nickel and acid as the solutions with the promoting metals.

TABLE 2

Postprecipitation of nickel sulfide with copper sulfide at 80°C.

Total volume, 35 ml. Amount of copper sulfide, 0.5 millimole; amount of nickel chloride, 1.25 millimoles. Time of shaking, 19 hours

Hydrochloric acid concentration (<i>N</i>)	0.05	0.08
Nickel precipitated in per cent*	58	52

* Blanks run in the absence of copper showed no nickel precipitated.

From the first set of experiments (blank) it is seen that nickel sulfide in the absence of promoting sulfides is formed very slowly in 0.004 *N* hydrochloric acid. The induction period is relatively long. After the precipitation has started the nickel sulfide promotes its own precipitation, the precipitation curve being typical of an autocatalytic process. At hydrochloric acid concentrations of 0.01 *N* or greater the induction period in a pure nickel chloride solution is so long that no precipitate of nickel sulfide occurred in the time during which the experiments were run.

It is evident that nickel sulfide is postprecipitated with copper, mercuric, and zinc sulfides. Particularly from the experiments of set 2 it is seen that the induction period is relatively long in the presence of the promoting sulfides and that the postprecipitation curves are typical again of an autocatalytic process. Mercuric sulfide has a stronger effect on the postprecipitation than copper sulfide. The relative effect of zinc sulfide varies with the acid concentration. In set 1 the zinc sulfide is formed from neutral solution, the final acid concentration being 0.004 *N*. Under these conditions the zinc sulfide formed is extremely finely

divided, and its effect is greater than that of mercuric sulfide. In set 2 the zinc sulfide is somewhat coarser (final acid concentration 0.01 *N*), and its effect equals that of mercuric sulfide. With increasing acidity of the solutions (sets 3 and 4) the zinc sulfide becomes coarser. In set 4 (0.05 *N* acid) the zinc sulfide formed is so coarse that it does not promote the precipitation of nickel sulfide at that acidity.

A few experiments were carried out on the postprecipitation of nickel sulfide with copper sulfide at 80°C. The results are given in table 2. The flasks containing the solutions were placed on the gravel in the hot room (temperature about 80°C.). A slow stream of hydrogen sulfide saturated with water vapor at this temperature was passed through the flasks for 19 hours. After this period the mixtures were filtered and the filtrates analyzed for nickel. The few results show that the rate of postprecipitation with copper sulfide is much greater at 80°C. than at room temperature.

SUMMARY

It has been shown that nickel sulfide postprecipitates with the sulfides of copper, mercury, and zinc, the effect of mercuric sulfide being greater than that of copper sulfide. The relative promoting effect of zinc sulfide greatly depends upon the acidity at which it is separated from solution. The rate of postprecipitation with copper sulfide at 80°C. is much greater than at room temperature. Nickel sulfide autocatalyzes its own precipitation.

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THE CHEMICAL EFFECT OF ELECTRICAL DISCHARGE IN GASEOUS HYDROCARBONS. IX

THE CONDENSATION OF ETHANE, PROPANE, BUTANE, AND PROPYLENE AS A FUNCTION OF TIME, AND COMPARISON OF RATES OF CONDENSATION OF LOWER MEMBERS OF THE PARAFFIN, OLEFIN, AND ACETYLENE SERIES¹

S. C. LIND AND GEORGE R. SCHULTZE²

School of Chemistry, University of Minnesota, Minneapolis, Minnesota

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INTRODUCTION

In two previous papers (8, 9) of this series are reported the results obtained in the electrical condensation of gaseous hydrocarbons. These papers include work on the condensation of methane, ethylene, and acetylene and the changes which they undergo when exposed for different lengths of time to electrical discharge in an all-glass ozonizer system. Further investigation of electrical discharge in ethane, propane, butane, and propylene has been undertaken in order to extend the present knowledge concerning the nature of electrical condensation and to enable us to make a comparison of the rates of condensation for the lower hydrocarbons of the paraffin, olefin, and acetylene series. From this comparison certain conclusions are drawn as to the factors which govern the rate of electrical condensation of the hydrocarbons.

EXPERIMENTAL PROCEDURE

The apparatus and experimental procedure are described in detail in the previous papers (8, 9). For the sake of clarity we briefly repeat that the gases, after repeated distillation, were admitted to the discharge chamber, which was an all-glass Siemens tube.

In order to obtain comparable results, the same amount of gas was taken for each experiment and the same electrical conditions were applied, the current being kept constant at 6 amperes and 89 volts in the primary circuit and approximately 16,300 volts in the secondary circuit. After the runs the gases were completely analyzed by low-temperature fractiona-

¹ This paper includes part of an investigation on "The Effect of Electrical Discharge upon Gaseous Hydrocarbons," which is Project 8 of American Petroleum Research. Financial assistance was received from the Research Fund of the American Petroleum Institute, which was donated by the Universal Oil Products Company.

² Research Associate.

tion and the individual gases were identified, the unsaturates by means of liquid absorption in potassium permanganate or bromine water, and the saturates by combustion in a Hempel explosion pipet.

The interpretation of the individual analyses often is very difficult, although a great deal of experience has been acquired with regard to the analytical problems involved. The analysis of the reaction products was found to be increasingly troublesome for increasing molecular weight of the initial gas.³ Hence these difficulties ought to be kept in mind when considering certain discrepancies in the analyses, since a few cubic centimeters of gas mixture to be analyzed have frequently proved to contain all individual representatives which conceivably could be present. It is for this reason that some experiments were repeated several times, in order to show the limits of error and to guarantee a reliable average.

During the course of investigation the ozonizer had to be replaced once. All experiments of this paper except those made with ethane were carried out in the new reaction chamber. The results thus obtained were correlated with the previous results by means of text experiments with ethylene, which showed that *ceteris paribus* a run of 24.5 minutes corresponds most closely to a run of 20 minutes in the old ozonizer, as judged by the pressure drop and by the analysis of final products. The experiments of 60 minutes' duration were accordingly extended to 73.5 minutes.

RESULTS

Ethane

The gas was taken from a tank and redistilled. Vapor pressure measurements checked the results of previous investigators within the limits of error. A total combustion proved its purity. The same care was taken in all the following experiments. The actual pressure changes during the run are omitted.⁴ Table 1 shows the results of two runs of 20 minutes' duration and of three runs of 60 minutes' duration.

In spite of smaller discrepancies the following conclusions are arrived at with certainty:

(1) A small and definite increase in pressure takes place during the run. This is seen from the ratio of cubic centimeters of final gas to cubic centimeters of initial gas. This pressure increase is of course obvious at once from the actual pressure data, a typical set of which is here reproduced in

³ This is mostly due to mutual solubility of the liquefied gases, which makes the selection of proper temperatures for the cuts a rather arbitrary matter. Furthermore the liquid-gas mixture must be heated several times to much higher temperatures and cooled down again in order to assure a complete recovery of the gas which is to be distilled. Experiments not only with different gases but also for different lengths of time are required to warrant good results.

⁴ These data are, however, available to anyone interested.

table 2. Attention is called to the fact that the apparent maximum which was previously reported for the similar reaction with methane (8) completely disappeared when the proper pressure reductions were applied.

(2) In agreement with this increase in pressure unsaturated compounds, —acetylene and ethylene,—are formed in the gas phase. There is, however, no evidence of the presence of propylene or higher unsaturates.

TABLE 1
Condensation of ethane under electrical discharge
Results and comparison for 20-minute runs and 60-minute runs

	20 MINUTES		60 MINUTES		
	Run a	Run b	Run a	Run b	Run c
Initial gas taken (cc. at N.T.P.)	268.6	269.8	258.7	257.7	267.9
Initial pressure (reduced)	495.6	489.9	474.5	475.5	490.3
Time of run (minutes)	20	20	60	60	60
Final pressure (reduced)	505.1	503.2	491.7	500.4	513.0
Final gas (cc. at N.T.P.)	274.0	274.0	263.9	272.0	275.5
Analysis of final gases (cc. at N.T.P.):					
CH ₄	6.7	6.9	11.8	17.0	17.5
H ₂	23.3	21.7	57.3	80.5	69.5
C ₂ H ₂	2.0	0.5	3.0	4.8	3.7
C ₂ H ₄	2.0	2.7	6.5	6.7	7.1
C ₂ H ₆	228.0	221.0	164.9	137.4	151.3
C ₃ H ₈	6.8	8.8	13.6	18.9	15.4
C ₄ H ₁₀	1.9	2.5	6.6	2.6	6.1
C ₆ H ₁₂ and higher	0.6	1.5	Traces	1.2	1.6
Total	271.3	265.6	263.7	269.1	272.2
Ratio of $\frac{\text{cc. of final gas}}{\text{cc. of initial gas}}$	1.02	1.02	1.02	1.06	1.03
H ₂ /(CH ₄ + H ₂)	0.78	0.76	0.83	0.83	0.80
—Hydrocarbon/H ₂	1.74	2.25	1.64	1.50	1.68
Formula of liquid calculated from atomic balance sheet	C _n H _{2.2n}	C _n H _{2.4n}	C _n H _{2.2n}	C _n H _{2.1n}	C _n H _{2.2n}
Liquid conversion (per cent)	6.2	7.2	16.3	23.2	20.4
Total hydrocarbon reacted (per cent)	15.1	18.1	36.2	46.7	43.5
Average	16.6		42.1		

(3) The percentage of hydrogen in the methane-hydrogen fraction does not change appreciably for different lengths of time. The absolute values lie somewhat lower than are found for ethylene, which is in agreement with the earlier investigations (7).

(4) The ratio of —H.C./H₂ drops off from 2.0 to 1.6 to 1.4 for 20 minutes, 1 hour, and 8 hours, respectively (6). The same drop holds in general for the condensation of saturates, although the validity of this

statement may be somewhat hidden on account of the fluctuations apparent in the present case (cf. table 4). This change of the ratio is mostly due to the decrease in reaction velocity, while the slight increase in hydrogen production for longer runs acts in the same direction.

TABLE 2
Condensation of propane under electrical discharge
Results and comparison for 24.5-minute runs and 73.5-minute runs

	24.5 MINUTES		73.5 MINUTES	
	Run a	Run b	Run a	Run b
Initial gas taken (cc. at N.T.P.)	270.0	262.7	270.0	270.0
Initial pressure (reduced)	501.8	491.2	506.8	508.1
Time of run (minutes)	24.5	24.5	73.5	73.5
Final pressure (reduced)	528.8	516.4	563.7	569.4
Final gas (cc. at N.T.P.)	284	274.2	296.5	300.0
Analysis of final gases (cc. at N.T.P.):				
CH ₄	6.1	7.8	27.8	30.2
H ₂	16.0	15.4	51.6	60.8
C ₂ H ₂			5.4	4.9
C ₂ H ₄	Traces		6.1	7.4
C ₂ H ₆	3.6	1.2	5.7	8.3
C ₃ H ₄				
C ₃ H ₆	13.2	16.8	15.5	19.1
C ₃ H ₈	236.8	227.7	172.7	161.0
C ₄ H ₁₀	4.1	3.5	6.8	6.2
C ₄ H ₁₂	1.6	1.2	0.8	Traces
Total	281.4	273.6	292.4	297.9
Ratio of $\frac{\text{cc. of final gas}}{\text{cc. of initial gas}}$	1.05	1.05	1.10	1.11
H ₂ /(CH ₄ + H ₂)	0.72	0.66	0.65	0.67
— Hydrocarbon/H ₂	2.07	2.27	1.88	1.79
Formula of liquid calculated from atomic balance sheet	C _n H _{2.2n}	C _n H _{2.6n}	C _n H _{2.1n}	C _n H _{2.1n}
Liquid conversion (per cent)	2.7	3.1	18.1	20.6
Total hydrocarbon reacted (per cent)	12.3	13.3	36.0	40.4
Average	12.8		38.2	

(5) The formula calculated for the liquid shows no decisive change as the length of the runs increases. The liquid appears to be slightly richer in hydrogen than the liquid obtained from methane. It should, however, be remembered that the formula of the liquid bears all errors of the analysis, since it is obtained from an atomic balance by difference. This makes any definite statement about changes in this formula rather doubtful, in particular for runs shorter than 60 minutes.

(6) As may be seen from the "total hydrocarbon reacted" the condensation has begun to slow up before the expiration of the 60-minute interval: the amount of ethane reacting has just begun to drop below the proportionality relationship.

(7) Contrary to (6) the liquid production seems to be still proportional to the time. This means that the condensation to liquid must be first delayed or later speeded up, either assumption being identical with an induction period for the first stage of reaction. The induction period is not so pronounced, however, as was found for methane. The fact that the absolute amounts of hydrocarbons produced, e.g., methane, still increase between 20 and 60 minutes further supports this idea and proves incidentally that this induction is not complete in 20 minutes. This long duration of the induction period also tends to make the distinction between the main stage of reaction and the induction period somewhat indefinite.

(8) Relatively large amounts of propane are formed. This lends further support to the conclusion that for both electrical and alpha-ray condensation there is a closer relation between ethane and propane as well as between ethylene and propane than exists between ethylene and ethane. This is in agreement with earlier investigations (8, 9).

Propane

In the analyses difficulties were encountered for the first time in the determination of unsaturates in mixtures with higher hydrocarbons by means of bromine water. The latter was found to react distinctly with propane, thus invalidating the results of several runs before the reason for the discrepancies was located. An aqueous (3 per cent) solution of potassium permanganate finally gave satisfactory results (12). The results of the propane runs as compiled in table 2 may be summarized as follows: (1) The pressure increase appears to be real and is still more pronounced than for ethane. This is in line with earlier investigations (5). (2) The pressure increase would be explained by the presence of unsaturated hydrocarbons in the gas phase. These were actually found. (3) Here again the percentage of hydrocarbon in the fraction of methane-hydrogen produced appears to be constant for different lengths of time. (4) The hydrogen production, in relation to the total hydrocarbon reacted, and the liquid formula show the same general principles as pointed out for ethane when the length of runs is changed. The former drops slightly; the latter appears to be constant for increase in time. (5) A comparison of the liquid production and the total hydrocarbon reacted shows again that there is no direct relation between the two values. An induction period is evident from such a comparison. (6) Contrary to what would be expected is the fact that the action on propane is still proportional to the time for 73.5 minutes. In this connection it must be men-

tioned that propane is the only gas which does not fit into the general scheme, which is discussed more fully in connection with table 7. This is the more surprising as there is no evidence of other irregularities within the propane experiments or when propane is compared with other hydrocarbons.

n-Butane

The condensation of this gas furnishes such great difficulties in many respects that any too definite assertion would appear precarious. This

TABLE 3
Condensation of butane under electrical discharge
Preliminary results of one run of 24.5 minutes' duration

Initial gas taken (cc. at N.T.P.)	273.3
Initial pressure (reduced)	512.8
Final pressure (reduced)	550.3
Final gas (cc. at N.T.P.)	286.8
Analysis of final gas (cc. at N.T.P.):	
CH ₄	10.5
H ₂	15.6
C ₂ H ₂	
C ₂ H ₄	1.1
C ₂ H ₆	5.0
C ₃ H ₄	
C ₃ H ₆	18.1
C ₃ H ₈	48.4
C ₄ H ₆	
C ₄ H ₈	5.0
C ₄ H ₁₀	179.5
C ₆ H ₁₂	1.4
Total	284.6
Ratio of $\frac{\text{cc. of final gas}}{\text{cc. of initial gas}}$	1.05
H ₂ /(CH ₄ + H ₂)	0.60
- Hydrocarbon/H ₂	6.0
Formula of liquid	C ₄ H _{2.25}
Liquid conversion (per cent)	11.3
Total hydrocarbon reacted (per cent)	34.3
Average of all experiments on butane up to now	32.9

was partially caused by the fact that, in spite of many distillations, the initial gas could not completely be freed from its isomer without application of a special distillation column which was not yet available. Isobutane remained to an extent of approximately one-fourth of the total. Moreover, isobutane seems to be formed under the influence of discharge. Its presence interferes greatly in separating the propane fraction from the

butane fraction on account of its high vapor pressure. Chemical methods for separation which are reported in the literature, e.g., use of sulfuric acid of different strengths, have not yielded satisfactory results in our experiments. Therefore, from a good many data, only one run of 24.5 minutes' duration is reported in table 3. It gives an estimate of those data which are most urgently desired, and shows a general analogy to the other paraffin hydrocarbons investigated. One experiment was carried out using isobutane as initial gas. The isobutane was obtained from the attempted separation of this gas from butane (see above) and contained approximately 10 to 15 per cent of normal butane. The gas did not show

TABLE 4

Comparison of average values obtained from all experiments

(a) For 20 minutes

	CH ₄	C ₂ H ₆	C ₃ H ₈	C ₄ H ₁₀
(1) Pressure increase (per cent).....	0	2	5	7
(2) H ₂ /(CH ₄ + H ₂).....		0.78	0.69	0.61
(3) -H.C./H ₂	1.47	2.01	2.17	5.85(?)
(4) Liquid formula.....	Approximately C _n H _{2.1n}			
(5) Liquid conversion (per cent).....	1.1	6.7	2.9(?)	9.8
(6) Hydrocarbon reacted (per cent).....	7.9	17.0	12.8(?)	32.9
(7) Number of runs.....	3	3	2	5

(b) For 60 minutes

	CH ₄	C ₂ H ₆	C ₃ H ₈	C ₄ H ₁₀
(1) Pressure increase (per cent).....	0	4	11	
(2) H ₂ /(CH ₄ + H ₂).....		0.82	0.66	
(3) -H.C./H ₂	1.35	1.61	1.83	
(4) Liquid formula.....	Approximately C _n H _{2.1n}			
(5) Liquid conversion (per cent).....	7.5	20.0	19.4	
(6) Hydrocarbon reacted (per cent).....	23.1	42.1	38.2	
(7) Number of runs.....	3	3	2	0

any appreciable differences as compared with its isomer, which further supports the conclusion of Schoepfle and Fellows (11), based on the octanes, that straight-chain and branched-chain compounds behave essentially in the same manner when exposed to cathode rays. However, the variations in working with these gases are still so large that an improved method may well bring out minor differences which are not detected at the present time.

In table 4 the average values of all experiments without any exception are compiled for comparison. Values which are out of line are marked with a question mark. The high value of the ratio -H.C./H₂, which was found throughout the butane experiments, should not be taken too

seriously, as it might be explained by the difficulties still inherent in these runs.

The low values for liquid production and reaction yield of the propane runs were mentioned above.

Furthermore, the differences and fluctuations in the formula of the liquid should be strongly questioned. Since it is based upon a difference method, the limits of error of each cut of the gas analyses will reappear in the atomic balance, which deprives the formula of a great deal of its significance. As the amount of gas reacted increases and hence the relative error of the analyses decreases with increasing lengths of runs, the liquid formula is more accurate for the 60(73.5)-minute runs than for the 20 (24.5)-minute runs. The only conclusion which appears to be justified is that the liquid shows the same or approximately the same composition regardless of the differences in time of exposure or in the nature of the paraffin used. Therefore the most probable value only is given.

For $\text{H}_2/(\text{CH}_4 + \text{H}_2)$ no value is given in the methane column, since methane is the initial gas of the experiment.

For butane, no runs of longer duration than 24.5 minutes are as yet available.

It is evident that there is no direct relation between liquid production and hydrocarbon reacted.

The pressure increase for different lengths of time as well as for increasing molecular weight of the initial gas is clearly evident from the comparison in this table.

Many conjectures may be made as to the correct interpretation of the second and third horizontal columns in tables 4a and 4b. Since the higher paraffins are acted upon more readily than the lower ones, the continuous increase of the ratio $-\text{H.C.}/\text{H}_2$ is not surprising. The absolute hydrogen production per unit time appears to be approximately constant.

Propylene

The propylene runs are properly compared with the ethylene runs as previously (10) reported. From the analytical standpoint they involve considerably more difficulties than those made with ethylene.

We are greatly indebted to Dr. R. R. Palmer who made the 24.5-minute run in table 5 for us. As the experiment was undertaken with the main purpose of finding out the exact amount of hydrocarbon reacted for 24.5 minutes, a detailed analysis was avoided. For longer times the analysis of the final gases is somewhat easier.

The following conclusions may be drawn from table 5: (1) The condensation of propylene shows a distinct decrease of pressure, as was found for ethylene also. (2) While the formation of acetylenes plays a minor rôle in the case of saturated hydrocarbons, it is more pronounced for the

olefins, —for ethylene as well as for propylene. The analysis of the 24.5-minute run, however, shows more acetylene than would be expected. (3) Both the "liquid conversion" in connection with the "total hydrocarbon reacted" and especially the slow start of pressure drop at the beginning of the experiments indicate the existence of an induction period. (4) The

TABLE 5
Condensation of propylene under electrical discharge
Results and comparison for 24.5 minutes and 73.5 minutes

	24.5 MINUTES	73.5 MINUTES	
	Run a	Run a	Run b
Initial gas taken (cc. at N.T.P.).....	270.3	260.3	265.7
Initial pressure (reduced)	503	486.6	494.0
Time of run (minutes).....	24.5	73.5	73.5
Final pressure (reduced).....	432	222.6	216.0
Final gas (cc. at N.T.P.).....	236.7	112.0	109.4
Analysis of final gases (cc. at N.T.P.):			
•CH ₄	4.8	15.0	17.2
H ₂	14.0	41.4	41.3
C ₂ H ₂	23.8(?)	6.2	4.4
C ₂ H ₄		3.0	3.5
C ₂ H ₆	14.4	4.4	6.4
C ₃ H ₄		?	?
C ₃ H ₆	140.0	15.0	13.3
C ₃ H ₈	16.9	14.0	17.8
C ₄ H ₆		0.4(?)	?
C ₄ H ₈		1 (?)	?
C ₄ H ₁₀	18.1		
C ₅ H ₁₂	2.8	4.3	1.8
Total.....	234.8	112.2	110.5
Ratio of $\frac{\text{cc. of final gas}}{\text{cc. of initial gas}}$	0.87	0.43	0.41
H ₂ /(CH ₄ + H ₂).....	0.75	0.73	0.71
— H.C./H ₂	9.3	5.9	6.1
Formula of liquid.....	C _n H _{1.5n} (?)	C _n H _{1.7n}	C _n H _{1.7n}
Liquid conversion (per cent).....	20.4	74.6	77.3
Total hydrocarbon reacted (per cent).....	48.2	94.2	95.1
Average.....		94.6	

formula of liquid agrees well with the results for ethylene. (5) The value of — H.C./H₂ = 6.0 and the ratio H₂/(CH₄ + H₂) = 0.7 are in agreement with the results of the ethylene runs.

In table 6 we have compiled for the sake of comparison the per cent hydrocarbon reacted for the runs reported in this communication together

with the corresponding results for methane, ethylene, and acetylene from Paper No. VII in this series.

For the alpha-ray condensation of hydrocarbons, the rates of condensation, i.e., the chemical yields (M) per ion pair (N), are represented by simple M/N ratios: the value of this constant for all saturated hydrocarbons so far investigated is equal to about 2; for all unsaturates it exceeds the value of 2, having the value of 5 for ethylene and even of 20 for acetylene. Since the ionization produced by electrical discharge hinges upon so many different factors in the conditions applied, one cannot expect that the chemical yield should appear to remain so nearly constant for different gases as was found for the methane homologs under influence of alpha-radiation. Taking the amount of hydrocarbons reacted as a measure of the chemical change produced in the gas, one finds that in electrical discharge also the rates of condensation are higher for unsaturates than for saturated hydrocarbons.

TABLE 6

Reaction produced in different hydrocarbons during 20 (24.5) minutes

HYDROCARBON TAKEN	PER CENT REACTED	NO. OF RUNS
Methane.....	7.9	3
Ethane.....	17.0	3
Propane.....	12.9	2
Butane.....	32.8	5
Ethylene.....	39.6	3
Propylene.....	65.0	1
Acetylene.....	75.5	4

Insofar as the saturated hydrocarbons are concerned, one would expect an increase in condensation for the higher members of the series, since the "stopping power" toward electrons may be assumed to increase with increasing molecular weight. This is verified by the experiments.

One sees that the facts obtained from a study of the lower hydrocarbons fit into the general scheme and extend our knowledge about ionization accompanying electrical discharge.

But even a more quantitative aspect was established. From Lind's (4) study, we know the number of molecules reacting per ion pair if alpha-rays are the ionizing agent. The molecular ionization, i.e., the product of total specific ionization and stopping power $k \times s$ in terms of Bragg's equations (1), is also well known.

In 1928 Lind suggested (3) that the product of the M/N ratio and the molecular ionization may give an explanation, considering the results of Hutchinson and Hinshelwood (2) in the electrical decomposition of ammonia and nitrous oxide.

We have applied the same ideas to our experiments. Pressure drop and change in the nature of the gas complicate the ideal conditions, as was pointed out above. Furthermore, the values of $k \times s$ undergo a continuous change, the more the reaction products with their own values of $k \times s$ enter into the reaction. However, one finds that these ideas approximate most closely the results obtained. Therefore, not the yield of chemical action (M/N) alone is decisive for the electrical discharge, but the product (M/N) $\times ks$ is the integrating factor which seems to govern the electrical condensation of hydrocarbons.

In order to bring out this principle most clearly the experimental values of condensation, as given in table 1, may be compared with the values obtained from the alpha-ray investigations by reduction of the former by an arbitrary factor 3.95. For example, 7.9 divided by 3.95 = 2, 17.0

TABLE 7
Comparison of the rates of condensation for different hydrocarbons

C ₂ H ₆					
M/N from alpha-ray work.....				5.5	19.2
Bragg's $k \times s$				1.7	
Experimental values from electrical discharge.....	7.9	12.9	32.8	48.0	75.5
Experimental values reduced to basis of $\left(\frac{M}{N}\right)_{\text{CH}_4} = 2$					
$\frac{M}{N} \times ks$					27.7

* This is arbitrarily set equal to 2 for methane, for the reasons set forth above.

divided by 3.95 = 4.5, etc. It is evident that a different energy input or a different ozonizer than was employed in our experiments would have resulted in different values of the per cent hydrocarbon reacted, but a proportional change would have been observed in all of the gases. That is to say, any set of conditions which would have given the experimental value for methane would have given 4.5 instead of 17 for ethane, etc. This justifies the division of the "experimental values" by a factor of 3.95 as given in the fourth horizontal column of table 7.

To what extent our claim appears to be justified may be seen from the last two horizontal columns in table 2. Only the results of the acetylene condensation and of the propane condensation do not follow these considerations. However, for acetylene there exists an inhibiting factor, the nature of which we have thus far been unable to detect. If the reaction is slowed up in some way, this must result in lowering the rate of condensa-

tion of this gas and hence may account for the discrepancy between the acetylene runs and the general results obtained. For propane, the value of 3.3 as obtained by the experiments is in disagreement with the general increase of the rate for increasing molecular weight as well as with the value of 6 expected from the quantitative evaluation of the results. Since no explanation can be given for this, the propane runs certainly remain out of line.

SUMMARY

1. The condensation of ethane, propane, butane, and propylene under influence of electrical discharge has been studied with special consideration of its dependence upon the time.

2. A number of principles, which shed further light upon the extremely complex nature of electrical condensations, have been derived from detailed analyses of the reaction products.

3. The decisive differences between saturated and unsaturated hydrocarbons place paraffins and olefins in two different groups. More comprehensive data are offered to substantiate the group characteristics of these gases with special reference to different lengths of time.

4. A comparatively long induction period is found for each one of the gases investigated.

5. A comparison of different rates has been given for the electrical condensation of methane, ethane, propane, butane, ethylene, propylene, and acetylene. The product of molecular ionization and of the chemical yield under alpha-radiation checks most closely the results obtained and is considered to be the governing factor for the electrical condensation of gaseous hydrocarbons.

The authors wish to thank Mr. John L. Wilson who assisted in this work as American Petroleum Institute Research Assistant.

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NEW BOOKS

Numerical Data on Radioactivity. Nuclear Physics. Transmutations. Neutrons. Positrons. By I. JOLIO-CURIE, B. GRINBERG, R. J. WALEN. Excerpt from Annual Tables of Constants. 57 pp. Paris: Gauthier-Villars, 1931-36.

This represents the data in the field of radioactivity and nuclear physics published during the period 1931 to 1936. Naturally most of the space is devoted to the new nuclear transmutations and to artificial radioactivity. Of the elements Nos. 1 to 30, only helium has not been transmuted, and only hydrogen, helium, beryllium, and chromium have not been shown to have artificial radioactive isotopes, though those for nickel and cobalt have not been positively identified. From No. 31 to No. 92 only nine elements of the non-radioactive elements have not been transmuted or made radioactive. In addition, new artificially radioactive isotopes have been produced from thorium and uranium.

S. C. LIND.

The Theory of the Properties of Metals and Alloys. By N. F. MOTT AND H. JONES. Oxford University Press, 1936.

The Theory of Metals. By A. H. WILSON. Cambridge University Press, 1936.

These two important books on the application of quantum mechanical theory to the theory of metals are both products of the school of younger English theoretical physicists. Both cover much the same territory, namely, the theory of the *electronic* properties of metals and alloys, and restrict themselves in the main to the mathematical theory. No attempt is made to survey the literature on the technical properties of the metallic state.

In spite of their similarity in scope, the two books differ considerably in emphasis and point of view. For the reader interested in obtaining a comprehensive treatment of the theory and its principal applications, with attention directed primarily to the successes of the theory rather than its limitations, the first volume, that of Mott and Jones, will probably be the more appealing. The first chapter gives a general discussion of the theory of the thermodynamic properties of the crystal lattice (specific heat and equation of state theory) and of the Bragg-Williams order-disorder theory of alloys, and is largely informative in nature. The second chapter gives a general treatment of the theory of electronic states in metallic lattices, with a good treatment of Brillouin zones. The bulk of the book is then devoted to various standard problems, magnetic properties, electrical resistance, etc. Attention may be called particularly to the discussions on cohesion, the resistance of liquid metals, and the various sections on alloys, all of which are largely absent from other books on the subject. The newer discussions of Slater on ferromagnetism and superconductivity are of course not treated. The discussion of the electrical resistance of bismuth, which has been contributed to the theory by Dr. Jones, will also be of special interest to some readers. This book can be recommended as one of the best and most informative works which has yet appeared in this field.

On turning to the volume by Dr. Wilson, we find the theory treated in a quite different spirit. Wilson adopts a much more critical attitude towards the theory, and writes not so much to inform the reader of its successful applications as to present a critical discussion of its foundations and method of approach to the prob-

lem in hand. The list of general topics studied is much the same as in the work of Mott and Jones, but the argumentation is much closer, which may make the book somewhat difficult reading for one without any particular previous acquaintance with the theory. It is not possible here to give any statement of the general criticisms which the author brings forth against the details of particular applications which have been made of the theory. On the whole these refer to well-known difficulties in the determination of the energy distribution of the electrons and the proper analysis of the lattice vibrations, particularly at low temperatures. The reviewer is quite in sympathy with the author, and believes that his discussion is a valuable contribution to the literature as well as a counterpoise to the prevailing tendency to overlook the deficiencies of the theory for the sake of its successes. It can only be hoped that it will soon be possible to remove at least some of its weaknesses and to put it on a firmer foundation.

E. L. HILL.

Reactivity of Solids (Reaktionsfähigkeit fester Stoffe). By J. A. HEDVALL. 243 pp.; 50 illus. Leipzig: Verlag Johann Ambrosius Barth, 1938. Price: 18 RM (paper); 19.20 RM (cloth).

The ancient dictum of Aristotle that "corpora non agunt nisi liquida," which means that only liquids can react, is quite wrong, since even in solids the atoms are in motion. Owing, however, to the slow diffusion velocity of atoms through the layer of reaction product, reactions of solids at low temperature are almost brought to a stop. For this reason such reactions have not been commonly recognized except by students of high-temperature phenomena.

Professor Hedvall, who has by his numerous researches made himself an authority in this field, points out that the weaker the forces holding the particles in their lattices the more easily will reactions occur, and every factor which weakens these forces will enhance the reactivity.

The book is divided into three parts. The first, which covers about one-fourth of the work, is concerned with the fundamental principles of crystal structure and with their relation to chemical composition. These developments have been of the greatest significance in the understanding of solid phase reactions. The various lattice types, ionic, molecular, metallic, layer, etc., are described and illustrated. The principles of polymorphism are discussed. A section is devoted to lattice energies and to lattice vibrations with their characteristic frequencies. An important discussion is given of surface properties of solids, in regard to recrystallization processes and to catalytic effects on mixed-oxide catalysts.

If the reader is already familiar with the general principles of crystal chemistry, he will undoubtedly find the second part of the book the most instructive. Part II covers more than one-half of the book. This second part treats of the historical developments in the subject of reactivity of solids, attention being given to experimental methods and to the deduction of the underlying principles. A systematic treatment is given of reactions involving ionic interchange (Platzwechselreaktionen) for bivalent oxides with sulfates, carbonates, phosphates, and silicates. The quantitative study of rates of gas-forming reactions by Braune, Jander, Fishbeck, and others is discussed. The pioneering work of Hüttig on the nature of intermediate phases is described in detail. The important studies of Hevesy, Phipps, Biltz, and others on electric conductivity and on diffusion in solids is presented and discussed to show the factors which determine ionic mobility in solids. The rôles of polymorphic change, radiation, etc., in loosening the lattice and permitting greater ease of atomic movement are described. The past history of an oxide, for example, whether formed from sulfate or carbonate, is shown to have great effect on its properties. Some discussion is given of fluorescence and phosphorescence.

The third part of the book should be of special value to ceramic and metallurgical workers. Reactions of glass melting, properties of certain refractories, and of certain calcined oxide colors are discussed. Some attention is given to the thermal properties of clays, chromite, dolomite, and other minerals. Sintering and grain growth in metal powders and catalysis of certain reactions by gas or liquid are also discussed.

In the writer's opinion this book marks a definite step forward in its field, for it brings together and treats systematically the observations and theories which hitherto have been scattered through many scientific journals. The book is well documented with literature references. Every worker who deals with the heat treatment of inorganic materials will find it full of stimulating ideas and concepts.

NELSON W. TAYLOR.

Experimental Food Study. By AGNES FAY MORGAN AND IRENE SANBORN HALL. 414 pp. New York: Farrar and Rinehart, Inc. Price: \$3.00.

This laboratory text, while designed for beginning students, is based upon organic and physicochemical principles in large part. Since the students who will use it will not ordinarily have had extensive training in the physical and biological sciences it follows, perforce, that the treatment accorded these principles has been made very simple and elementary.

Thus in the early portion of the text appears a discussion of the properties of solutions, including vapor pressure, boiling point, and the relation of such properties to cooking problems. Experiments which demonstrate these principles are outlined. Particular reference is made to sugar solutions and the fundamentals of candy making. This is followed by a discussion of the freezing point of solutions which, in turn, is tied into the practical applications made in ice cream production.

Chemical constitution and the descriptive biochemistry of the carbohydrates is covered briefly, and this is followed by a chapter on acidity, pH, and buffers.

In part II appears a chapter on the colloidal state, and also a discussion of emulsions and foams; in addition there are chapters on proteins, fats, and the principal classes of food materials. An appendix includes various useful tables of data, including the proximate analysis and the mineral and vitamin content of the common foods.

The text and the series of laboratory experiments, which are presented in problem form, should prove stimulating to the students and encourage them in the effort to relate culinary practices to fundamental scientific principles.

C. H. BAILEY.

The Properties and Functions of Membranes, Natural and Artificial. A General Discussion held by The Faraday Society. April, 1937.

This General Discussion represents the Fifth Colloid Meeting organized by the Colloid Committee of the Faraday Society, which also comprises representatives of other societies, among them mainly societies interested in physiology and biology. Intentionally, therefore, the biological side of the matter was emphasized and the properties and functions of natural membranes were extensively discussed. Though very many facts are known, they appear most complicated, sometimes even conflicting; only a few, more general, conceptions can be extracted. This fairly negative result need not be considered disappointing; biological processes are probably centered in natural membranes, may they actually be two-dimensional organs (cf. A. Krogh's introductory paper) or merely membranes of a markedly specialized permeability. Hence we would have to know much more about life in general to be able to say more essential things about natural membranes and their functions.

Preliminary conceptions of the structure of the plasma membrane are frequently discussed. Perhaps Bungenberg de Jong's idea (mentioned on p. 990) of a membrane made of an amphoteric coacervate containing lecithin and the ions of macromolecules and other substances, presumably arranged in a special way towards the lecithin layer, would have deserved to be more thoroughly treated. Staudinger's interesting suggestion (Ann. 474, 161 (1929)) that hormones and vitamins may act in such very small amounts because they change the permeability of a membrane, a conception fitting Bungenberg de Jong's membrane model well, also does not appear to be mentioned.

Among the lectures concerning artificial membranes Elford's contribution is outstanding. He describes the method for making uniform collodion membranes of graded porosities and their use as ultrafilters. His table on p. 1103, containing the diameters of small particles of biological importance, from bacilli (*Bacillus prodigiosus* 750 $m\mu$) to the molecule of egg albumin (4 $m\mu$), with the viri and phages between 250 and 10 $m\mu$, shows impressively that the latter are established as a new type of colloidal state.

H. FREUNDLICH.

TITANIUM OXIDE HYDROSOLS. SOME RELATIONSHIPS TO OXIDE HYDROSOLS OF ZIRCONIUM AND THORIUM

HARRY S. OWENS AND ROBERT MORRIS

Department of Chemistry, University of Idaho, Moscow, Idaho

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Thomas and his coworkers have made numerous contributions to the literature of hydrous oxide hydrosols, explaining their reactions on the basis of polyolated structures. Since their work has been reviewed (10) recently it is unnecessary to discuss in this paper evidence in favor of the Thomas complex compound theory. However, two papers on basic thorium chloride (4) and basic zirconium chloride (6) hydrosols illustrate striking differences in the chemical reactions of these hydrosols when aged or when heated and then allowed to age; it seems advisable to mention these before giving the purpose of this investigation.

Basic thorium chloride hydrosols age rapidly and come to equilibrium in two months. Boiling the freshly prepared sols increases the acidity to a relatively high degree, with equilibrium being reached in 10 hours. When such heated sols are cooled and allowed to stand at room temperatures, there is a tendency for the acid produced to reverse the reaction so that the degree of acidity approaches the same values as those of the unheated sols aging at room temperature. Basic zirconium chloride sols, on the other hand, age slowly but continuously for periods as long as eight months, if not longer. On boiling, the pH values decrease rapidly for a short time, then more slowly for at least 240 hours. The heated sols, when cooled and allowed to stand, remain at the pH values attained with no tendency to become less acid.

These differences were ascribed to the less metallic nature of zirconium, which ionizes to only a small extent as the quadrivalent ion and tends to form basic radicals. The oxygen bridges in these radicals are very resistant to the action of acids like hydrochloric acid, which contain anions having low penetrating power. Consequently there is little or no tendency for the chloride ion to penetrate the complex, thus breaking the oxo bridges, or for the hydrogen ion to unite with oxo bridges to form ol groups.¹

Titanium, occurring in a still lower position of the periodic table, is even

¹ Schmid (1) has found that in very concentrated solutions of hydrochloric acid some oxonium salts are formed with zirconium oxychloride, but he found little or no evidence for the formation of zirconium tetrachloride.

less basic than zirconium. Therefore it seemed that it would form oxide hydrosols in which the micelles would contain mainly oxo bridges. The purpose of this paper is to submit evidence in support of this postulation.

TABLE 1
Composition of hydrosols

SOL	pH VALUE	Ti	Cl	EQUIVALENT RATIO Ti/Cl
		milliequivalents	milliequivalents	
T1.....	2.7	120	9	13.4
T2.....	2.7	88	8	11.0
T3.....	2.0	400	23	17.4

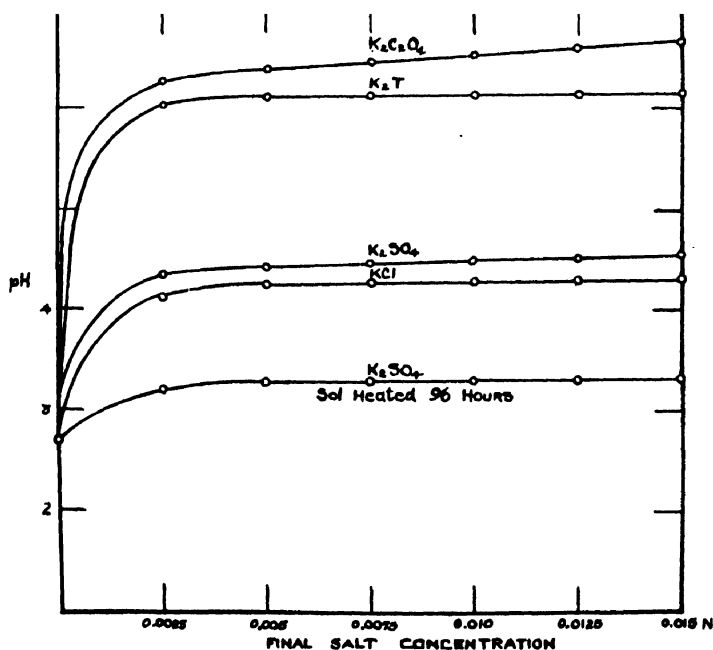


FIG. 1. Effect of potassium salts on sol T2

EXPERIMENTAL

Preparation and composition of the hydrosols

Hydrated titanium oxide was precipitated from titanium chloride solutions by addition of a slight excess of ammonium hydroxide. Centrifugal washings and decantations were used until the oxide was free from chloride. A portion of this material was peptized in boiling dilute hydrochloric acid to prepare sol T2. Another portion was peptized in dilute hydrochloric acid at room temperature to prepare sol T3.

Sol T1 was prepared by adding dilute ammonium hydroxide dropwise to a dilute solution of titanium tetrachloride until half the possible acid was neutralized. This sol was dialyzed for 148 hours.

Table 1 shows the composition of these three sols, which are typical of the eight run during the course of the investigation.

Action of neutral salts

The method used to study the effect of added neutral salts on the pH values of the hydrosols is essentially the same as that previously described (4). Figure 1 illustrates the results obtained with sol T2, which is typical of all those run. The order of effectiveness of the added anions to raise the pH value is oxalate > tartrate > sulfate > chloride. This order, while less complete, is the same as that obtained by Stewart (2).

TABLE 2

Effect of heating titanium oxide hydrosols

(a) sol T2

(b) sol T3

TIME OF HEATING	pH	TIME OF HEATING	pH
hours		hours	
0	2.7	0	2.0
1	2.7	24	2.0
10	2.7	48	2.0
24	2.7	96	1.9
48	2.7		
96	2.7		

Effect of heating

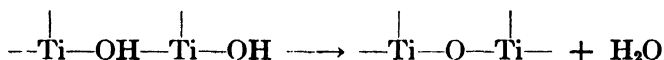
The effect of heating was studied in the same manner as with the basic zirconium chloride sols (6). The results are given in table 2. The effect of heating on the action of the sol with potassium sulfate is shown in figure 1.

DISCUSSION

Titanium oxide sols react in some ways like basic zirconium chloride and basic thorium chloride hydrosols. For example, the order of effectiveness of anions in raising the pH values of the sols is the same for the few salts run. Also the tartrate, if allowed to remain in contact with the precipitate originally produced on addition to the sol, will peptize the precipitate to form a titanate hydrosol. But there the similarities seem to end and differences are the rule.

The effectiveness of the anions might be in the same order, but the magnitude of the effect is not nearly so great. If the increases in the pH values are compared with the results obtained by von Wicklen (8) with dilute

hydrochloric acid and neutral salt solutions, one finds that there must be little displacement of hydroxo groups and most of the pH change comes from simple buffer action. This is borne out by experiments on heating in which the pH values of the sols remain practically constant even after 96 hours heating. If there were many hydroxo or ol groups present, there should have been some tendency for the formation of oxo bridges through ordinary oxolation with the concomitant increase in acidity. The absence of any increase in acidity on heating, accompanied by a decrease in reactivity of the sol with neutral salts, indicates that oxo bridges are formed through the following reaction.



From the facts presented it seems logical to conclude that the micelles in these titanium oxide hydrosols are composed mainly of titanium oxide.² This conclusion agrees with the findings of Weiser and Milligan (9).

However, even with these, the simplest of the oxide hydrosols yet studied from this point of view, the conclusion should not be drawn that chemical reactions are completely obviated. There is to be explained, besides the displacement of hydroxo groups, the reaction with tartrate forming negatively charged micelles. This is done nicely by assuming chelation, such as occurred with basic zirconium chloride (7), basic thorium chloride (5), and basic beryllium salt hydrosols (3). Stewart (2) in his investigation of titanium oxide hydrosols agrees with this explanation.

SUMMARY

Micelles in titanium oxide hydrosols are mainly titanium oxide with few hydroxo or ol groups in the complex. This conclusion is drawn from the small change in pH values obtained on adding neutral salts or heating titanium oxide hydrosols. The result is entirely in accordance with the Thomas theory of colloidal oxides when the position of titanium in the periodic table is considered.

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² Water of hydration has not been considered, although it must be present to allow irregular series formation with potassium tartrate.

NEUTRONS BY ALPHA-PARTICLE BOMBARDMENT OF LIGHT ELEMENTS¹

C. S. COPELAND² AND S. C. LIND

School of Chemistry, University of Minnesota, Minneapolis, Minnesota

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In view of the widespread interest in neutrons, it was felt that it might be of interest to examine the light elements under the same experimental conditions with respect to their neutron emission under α -particle bombardment, using radon as the source of α -particles.

For detection of the neutrons, it was decided to use the radioactivity induced in iodine. This element is one which is strongly activated by neutrons, and forms a single radioactive isotope, I^{128} , with a very convenient half-period of 25 minutes. By the use of ethyl iodide and the method of Szilard and Chalmers (5), the activity induced in a very large quantity of iodine can be concentrated and easily measured.

It must be admitted that the activity so obtained is not an absolute measure of the number of neutrons emitted by a given source, nor is the ratio of two activities produced by two different sources necessarily the ratio of the numbers of neutrons emitted by the two sources. This is because iodine (or any detector element) is not activated to the same extent by neutrons of different energies, and the energy spectrum of the neutrons emitted by different elements may vary widely. For a discussion of the difficulty of determining the absolute number of neutrons emitted by a given source, the reader is referred to the paper by Amaldi, Hafstad, and Tuve (1).

EXPERIMENTAL

The element, or compound of the element, to be examined was sealed, except where otherwise stated, with radon in a soft-glass bulb approximately 7 mm. in diameter. This bulb was kept in a soft-glass tube, sealed at one end, which could be dipped into ethyl iodide.

The radioiodine was prepared by placing the neutron source at the

¹ This paper was abstracted from a thesis submitted by C. S. Copeland to the Graduate Faculty of the University of Minnesota in partial fulfillment of the requirements for the degree of Doctor of Philosophy, June, 1937.

² Present address: Department of Chemistry, University of Southern California, Los Angeles, California.

the filter paper holding the silver iodide could be placed directly under the window.

The linear amplifier circuit was a standard circuit using the General Electric FP 54 Pliotron tube. The circuit is shown in figure 1. The circuit was shielded and the Pliotron tube was mounted in a brass case which could be evacuated. This case was equipped with a contact key (K in figure 1), so that the control grid of the tube could be grounded or floated at will. The floating grid method of measurement was used.

The radioactivity of the radioiodine was measured with respect to the activity of a standard radium tube (0.0036 mg. of radium) taken as unity. The radium standard was used in order to eliminate error arising either from variations in the sensitivity of the circuit or from variations in the pressure in the ionization chamber. It was proved experimentally that the relative activity of the radioiodine was independent of the pressure in the ionization chamber over the range of pressure used.

The value of the relative activity of the radioiodine, α_0 , at the time of removal of the neutron source was obtained by graphical extrapolation. The half-period was taken as 25 minutes. From α_0 , a quantity κ , proportional to the neutron emission per millicurie per second, was calculated by means of the equation

$$\kappa = \frac{\alpha_0(\lambda_1 - \lambda)}{M_0(e^{-\lambda_1 t} - e^{-\lambda t})}$$

where t is the time of irradiation of the ethyl iodide and M_0 is the number of millicuries of radon present at the start of the irradiation. λ_1 and λ are the decay constants of radioiodine and radon, respectively.

Since in most cases compounds and not pure elements were used as neutron sources, it was necessary to calculate the neutron emission which would have been observed if the pure emitting element, and not its compound, had been used. The appropriate conversion factor, μ , to make this calculation was obtained from the equation

$$\mu = \frac{\sum n_i Z_i^{2/3}}{n_e Z_e^{2/3}}$$

where n_i is the subscript of the i^{th} element in the formula of the compound and n_e is the subscript of the emitting element. Z is the atomic number.

DISCUSSION OF RESULTS

The results obtained for a number of substances are shown in table 1. In the column headed "neutron source" are given the elements or compounds which were sealed in glass bulbs with radon. In the case of compounds, the neutron emission given is for the compound as a whole. The last column gives the neutron emission on the basis that the emission for

TABLE 1

Neutron emission by various substances when bombarded by α -particles from radon

NEUTRON SOURCE	TIME OF IRRADIATION OF ETHYL IODIDE	M_0	α_0	κ	$\bar{\kappa}$	$\bar{\kappa}$ (Be=100)
	minutes					
Beryllium	218	34.6	30.0	157	157	100
	22	32.2	12.2	150		
	55	23.5	17.0	164		
Lithium carbonate	196	60.0	2.74	8.28	8.4	5.4
	223	47.7	1.82	8.36		
	83	46.3	2.04	8.75		
	137	40.6	2.13	8.04		
Boron (amorphous)	154	63.0	5.20	15.0	14.8	9.43
	235	49.4	4.13	15.1		
	93	47.9	3.54	14.2		
Calcium fluoride	224	79.8	8.70	19.8	19.5	12.4
	271	55.7	6.35	20.7		
	2912	53.7	3.80	17.9		
Sodium carbonate	397	104.3	4.35	7.69	6.9	4.4
	426	88.9	2.96	6.18		
	164	83.4	3.15	6.85		
Magnesium oxide	227	80.6	1.33	2.99	2.8	1.8
	315	76.8	1.18	2.81		
	266	37.3	0.51	2.5		
	256	31.2	0.48	2.8		
Aluminum (100-mesh filings)	293	69.1	2.55	6.71	6.8	4.3
	100	66.6	2.50	7.12		
	164	64.7	2.45	6.86		
	400	56.9	2.00	6.48		
Phosphorus (red)	370	59.1	0.49	1.6	1.6	1.0
	354	48.4	0.40	1.5		
Potassium chloride	324	59.1	0.56	1.9	1.7	1.1
	200	39.2	0.26	1.4		
Potassium carbonate	281	73.3	0.12	0.3	0.4	0.3
	179	70.1	0.16	0.4		
Calcium carbonate	316	79.6	0.17	0.4	0.4	0.3
	138	66.2	0.15	0.4		

 M_0 is the initial number of millicuries of radon in the neutron source. α_0 is the radioactivity of the silver iodide at the time of removal of the neutron source. κ is proportional to the neutron emission per unit time per millicurie of radon. $\bar{\kappa}$ is the average value of κ .

beryllium is 100. In addition to the substances listed in table 1, silica, sulfur, zinc, carbon, and paracyanogen were examined.

Silica was examined by sealing about 30 millicuries of radon in a fused quartz bulb. A very weak emission was observed. As nearly as could be judged, after allowing for the amount of radon used, the emission was of the same order of magnitude as the emission observed with the potassium and calcium carbonate sources.

Sulfur and zinc were examined under conditions somewhat different from those used for the other substances investigated. Flowers of sulfur and zinc dust were sealed with radon in Pyrex bulbs, and the ethyl iodide was irradiated in a 500-ml. round-bottom flask. The results so obtained were compared with the result observed when a Pyrex bulb containing aluminum and radon was employed.

Both the sulfur and zinc bulbs showed a weak emission of about the same order of magnitude. The emission was certainly less than one-tenth that obtained with an aluminum bulb.

The paracyanogen and carbon were both sealed in fused quartz bulbs. The ethyl iodide was irradiated according to the standard procedure, but the activity of the radioiodine was measured with a Geiger tube counter. This activity was compared with that produced by a Pyrex bulb filled with beryllium and radon. Taking the neutron emission for beryllium as 100, the emission for paracyanogen was approximately 0.9 and the value for carbon was approximately 0.4.

The above value for the neutron emission of paracyanogen is certainly too low. It was discovered after the radon had been introduced that insufficient paracyanogen had been used to fill the bulb, and, furthermore, a globule of mercury was accidentally introduced at the time the radon was collected.

Since an emission of about the same order of magnitude was obtained with calcium carbonate, potassium carbonate, sulfur, and zinc sealed in glass, carbon sealed in quartz, and an empty quartz bulb, it seems rather difficult to ascribe any significance to this emission from the standpoint of any particular element involved. Indeed, in those cases where glass bulbs were used, a weak residual emission might be expected, since an empty soft-glass bulb filled with radon shows a neutron emission of about 1.5 (beryllium = 100).

On the whole, in view of the results obtained, it would seem best to consider that there is a general background, and that all definitely positive results should be corrected for this background. Table 2 gives the values for the substances listed in table 1 after this correction has been made. In addition, in table 2 the corrected values of the neutron emission for the compounds listed have been converted into values for the active element involved. These results are shown graphically in figure 2.

TABLE 2

Corrected values of the neutron emission for the substances listed in table 1

NEUTRON SOURCE	κ	ACTIVE ELEMENT		
Lithium carbonate.....	5.1	Li	4.68	24
Beryllium.....	100	Be		100
Boron.....	9.1	B		9.1
Paracyanogen.....	0.5	N	1.90	1
Calcium fluoride.....	12.1	F	1.85	22.4
Sodium carbonate.....	4.1	Na	2.55	11
Magnesium oxide.....	1.5	Mg	1.76	2.6
Aluminum.....	4.0	Al		4.0
Phosphorus.....	0.7	P		0.7
Potassium chloride.....	0.8	Cl	1.93	1.5

κ is proportional to the neutron emission per second per millicurie of radon.

μ is the conversion factor by which the value of the neutron emission for a compound is multiplied to obtain the neutron emission of the active element in the compound.

$$\kappa' = \mu\kappa.$$

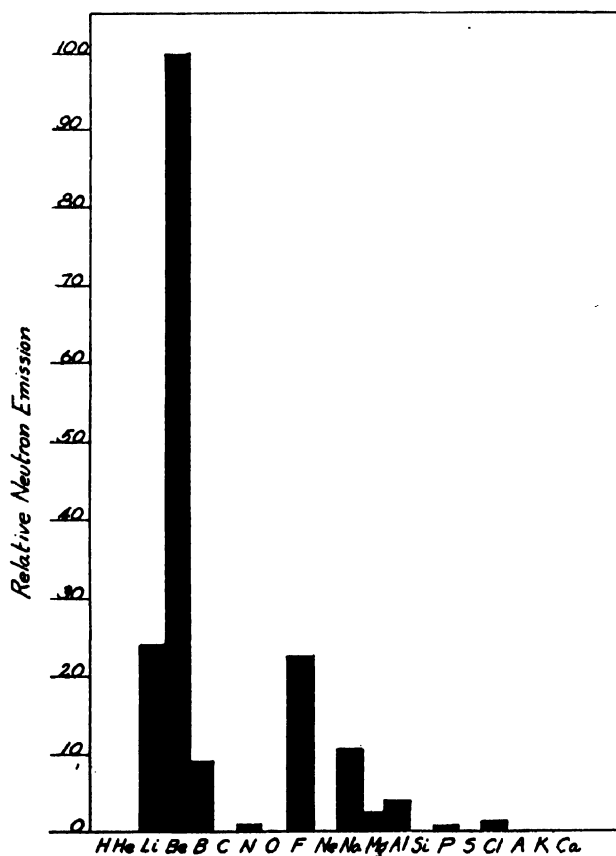


FIG. 2. Neutron yields from certain light elements (rare gases not investigated)

In the case of the oxides and carbonates listed in table 2, the neutron emission is ascribed to the metal involved, because of the weak neutron emission observed with potassium carbonate, calcium carbonate, and silica.

The neutron emission observed with paracyanogen is due to the nitrogen, since a similar carbon-filled bulb is a decidedly poorer neutron emitter. This is in agreement with the observation of Wertenstein (7) that nitrogen under RaC' α -particle bombardment produces radiofluorine.

In the case of potassium chloride, the active element is undoubtedly chlorine, because of the appreciable difference in neutron emission shown by potassium chloride and potassium carbonate. If potassium were the active element, we should expect the two compounds to show about the same neutron emission, since the conversion factor to potassium is 1.93 for potassium chloride and 2.07 for potassium carbonate.

The choice of chlorine as the neutron emitter in potassium chloride is given added weight by the recent work of Pollard, Schultz, and Brubaker (3), who showed that both argon and chlorine emit neutrons under ThC' and RaC' α -particle bombardment. The chlorine disintegration has been further studied by Hurst and Walke (2) and by Ridenour and Henderson (4), using artificially accelerated 11 Mev. and 9 Mev. α -particles, respectively.

With regard to a neutron emission from potassium, Zwyr (8) has shown, by studying the radioactivity induced in potassium chloride, that potassium must disintegrate with neutron emission under RaC' α -particle bombardment. Walke (6) has also investigated this reaction, using 11 Mev. α -particles, and has shown that both K^{39} and K^{41} disintegrate with neutron emission.

Our experiments would seem to show that the neutron emission from potassium under RaC' α -particle bombardment must be slight, since we were unable to detect any difference between potassium and calcium carbonates. Even if we assign all of the emission observed with potassium carbonate to potassium, the emission for potassium would only be approximately 0.5 per cent of that observed for beryllium.

SUMMARY

All of the elements from lithium through calcium, with the exception of the rare gases, have been investigated for neutron emission under α -particle bombardment. The α -particle source used was radon, and in each case the neutron yield was determined by measurement of the radioactivity induced in iodine. Positive neutron emission was observed for lithium, beryllium, boron, nitrogen, fluorine, sodium, magnesium, aluminum, phosphorus, and chlorine. The neutron emission from carbon, silica, sulfur, potassium carbonate, calcium carbonate, and zinc is less than 0.5 per cent of the emission from beryllium.

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STUDIES ON SILICA JELLIES. I

GELATION TIME AND CHANGE IN pH VALUE AS FUNCTIONS OF CONCENTRATION, INITIAL pH VALUE, AND TEMPERATURE¹

HAROLD W. BATCHELOR

Ohio Agricultural Experiment Station, Wooster, Ohio

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INTRODUCTION

An extensive literature on the properties of gels has accumulated since Pott (cited by Walden (14)) first prepared silica jellies in 1746, yet a diversity of opinion still exists regarding several important factors involved in their formation. A number of investigations have been conducted on sol-concentration (or dilution), hydrogen-ion concentration, and temperature as affecting the gelation time of inorganic sols, as well as on various factors affecting the gelation times of organic sols.

The general conclusions from such studies on silica sols may be summarized as follows: (1) Increasing concentration of sols reduces gelation time. (2) In solutions whose hydrogen-ion concentrations varied from pH 4.2 to pH 5.5, Hurd, Raymond, and Miller (5) found the log of the gelation time to be a lineal function of the initial pH value. Considerable confusion still exists regarding the hydrogen-ion concentration at which gelation takes place in minimum time. It may take place at neutrality or at slightly alkaline reactions. Apparently no observations on minimum time for gelation of slightly acid sols have been reported. (3) The change in pH undergone by a sol during and subsequent to gel formation is not well understood, since numerous conflicting and contradictory views have been expressed. The general opinion appears to be that gelation of acid silica sols is attended by little or no change in hydrogen-ion concentration, but in neutral and alkaline sols there is an increase in pH value. (4) Increasing temperature is generally regarded as reducing gelation time. (5) No single systematic study has yet been made of all these factors to determine their interrelations.

Silica gels, first proposed by Kuhne (7) as a base for bacteriological media, possess some characteristics which make them superior to other solid media. If prepared by mixing sufficiently dilute alkali silicates and

¹ A second paper dealing with the bacteriological phases of the work will be submitted for publication in the *Journal of Bacteriology*.

acid solutions to obviate the dialysis of excess salts, their ease of preparation and suitability for use are important in practical applications. The close regulation of pH desirable in the preparation of media and the importance of details essential to a uniform product with the desired characteristics are believed sufficient justification for a careful study of the factors involved. The present study has been concerned with gelation time and shift in pH value as affected by concentration (or dilution), initial pH value of the sol, and temperature during gelation. The data obtained permit a reconciliation of contradictory opinions regarding the behavior of silica sols and gels.

EXPERIMENTAL AND DISCUSSION

During the seven years that silica jellies have been used as bacteriological media in this laboratory, five brands of sodium silicate and two brands of potassium silicate have been studied. Potassium silicates are more satisfactory for the preparation of jellies that are not to be dialyzed, because the potassium ion induces gelation at lower concentrations than the sodium ion. For a given strength of jelly, therefore, potassium jellies may be prepared at a lower salt concentration than sodium jellies,—a matter of considerable importance in the use of bacteriological media. For this and other reasons to be noted elsewhere, potassium silicates have been studied more in this laboratory than sodium silicates. The work here reported has been confined to one brand of silicate, known as "Potassium Silicate Solution B630", manufactured by the Grasselli Chemical Company. Although stock solutions of silicates are usually prepared on the basis of specific gravity or of molarity of the solution, as a matter of convenience the solutions used in these studies were based on titrable alkalinity. As supplied by the manufacturer the potassium silicate is somewhat stronger than a 2 *N* alkali solution. The solutions were, therefore, diluted with an equal volume of freshly distilled water before attempting the standardization. To 10 ml. of this solution were added 100 ml. of distilled water and several drops of a 0.16 per cent solution of bromothymol blue. The silicate solution was then titrated with normal hydrochloric acid. From this titration the amount of water necessary to make the stock solution equivalent to normal hydrochloric acid was calculated and added. A second titration was then made and the solution further corrected if necessary. Manifestly, such a procedure could not be used for work in which absolute values were expected, since Weiser (15) has shown that titrations of colloids made in the usual stepwise manner require an appreciable lapse of time before equilibrium is reached. The method suffices, however, if only approximations are required. A 12-liter stock solution thus prepared was allowed to stand several weeks in a tightly stoppered bottle before being used. Aside from a slight brownish sediment

which probably consists of iron compounds, no changes in stored stock potassium silicates have been noted. Sodium silicates, on the contrary, tend to lose their silica by flocculation.

In the preparation of bacteriological media the use of several acids has been necessary to obtain an optimum ratio of anions for the growth of any particular organism. In the work here reported a mixture of 50 parts of normal sulfuric acid, 40 parts of normal hydrochloric acid, and 10 parts of 1.5 *N* orthophosphoric acid has been used. The proper compositions of the silicate-acid mixtures to give the desired initial pH values have been determined in the following manner. Sufficient distilled water was added to each of sixty-six 135-ml. screw-cap bottles to bring the total volume in each bottle to 100 ml. after the silicate and acid solutions had been added. As each solution was prepared it was thoroughly rotated by hand, and its pH value was determined by means of the Coleman glass electrode electrometer within 1 minute after the solution was prepared. The term "initial pH value" as used in this paper refers to the hydrogen-ion concentration of the sols determined under these conditions. The compositions of the

TABLE 1

Volumes of acid mixture per 10 ml. of potassium silicate to give initial pH value indicated

Initial pH value . . .	3.5	4.0	5.0	5.5	6.0	6.5	7.0	7.5	8.0	8.5	9.0
Volumes of acid mixture (ml.)	10.6	10.5	10.45	10.3	10.0	9.5		8.4	7.6	6.4	5.4*

solutions giving the desired initial pH values were derived from the titration curve thus obtained, and are given in table 1. The sols thus prepared to have initial pH values between 5.5 and 9.4 were found to be sufficiently well buffered for reproduction with considerable accuracy; the more acid sols presented greater difficulties in pH control. This may account for some of the inconsistencies in the data.

GELATION TIME AS A FUNCTION OF CONCENTRATION, INITIAL pH VALUE, AND TEMPERATURE

The precise point at which a sol passes into a gel cannot be defined, but an approximate determination by one of the numerous tests which are available may nevertheless be useful. In the absence of equipment required for the more precise optical methods, for the present study a device suggested by Sommer (11) has been employed. It consists of a mechanism by which several bottles are rotated at a slow uniform speed at an angle of about 30 degrees from the horizontal with a suitable provision for counting the number of revolutions of each bottle. The gelation time can be calculated from this number. Disturbance of the solution in validates

Smoluchowski's derivations (12, 13), but Flemming (2), Jableczyński (6), and others have found slight disturbances to have little or no effect. Under the conditions of these studies Sommer's device permitted an easy and, for the purpose at hand, a sufficiently accurate means of determining the gelation times.

The following procedure was strictly adhered to. At room temperature sufficient distilled water was added to each bottle to bring the solutions to the desired volumes after the silicate and the acid were added. The bottles were then placed in the water bath and allowed to come to the proper temperature. The stock solutions of silicate and acids were kept in the same water bath and were used only when the temperatures of the solutions were within the temperature limits allowed. After the addition of the silicate and of the acid mixture (added in that order) the bottle was rotated by hand to mix the solutions. It was then placed in the machine and the revolution counter was started. In each case record was kept of the time which elapsed from the moment the acid began to mix with the silicate until the automatic counter was engaged. All containers were kept tightly stoppered except when intentionally opened. For the 60° and 80°C. temperatures, the acid and alkali pipets were standardized to deliver a volume of solution equivalent to that delivered at room temperature (27°–28°C.), the temperature on which the initial pH values were based. In the absence of an accurate thermoregulator, the water bath was maintained within only $\pm 2^\circ\text{C}.$ of the desired temperature. Variations within the water bath were prevented by the use of an efficient stirring device.

Provision was made to determine the gelation times at temperatures of 20°, 40°, 60°, and 80°C., at initial pH values of 5.0, 5.5, 6.0, 6.5, 7.0, 7.5, 8.0, 8.5, and 9.0, and at total solution volumes of 50, 60, 70, 80, 90, and 100 ml. The ultimate concentrations of the solutions, estimated from the original stock normal silicate solution, therefore varied from 0.1 to 0.2 *N*, calculated as potassium. The actual pH values at which the jellies were formed at the higher temperatures are unknown, because the hydrogen-ion concentration is a function of temperature. In all probability they were more acid or less alkaline, as the case may be, than is indicated by the initial pH values determined at room temperature. Buchanan and Fulmer (1) have summarized the relations involved. Were water alone concerned in these studies, one might reasonably calculate the actual reactions of the solutions when raised to the higher temperatures, but one would scarcely be justified in making these calculations for solutions containing appreciable concentrations of electrolytes and of colloids. For the purpose at hand, this relation may be omitted from the remainder of the discussion. The data are shown graphically in figure 1.

If a three-dimensional figure, similar to that in figure 1, were pictured

as a typical isometric or dimetric drawing, an incorrect interpretation of the data might result. To prevent this, some deviations from usual conventions of drawing have been made. One may imagine that he is viewing this drawing from a point almost directly above and slightly to the right

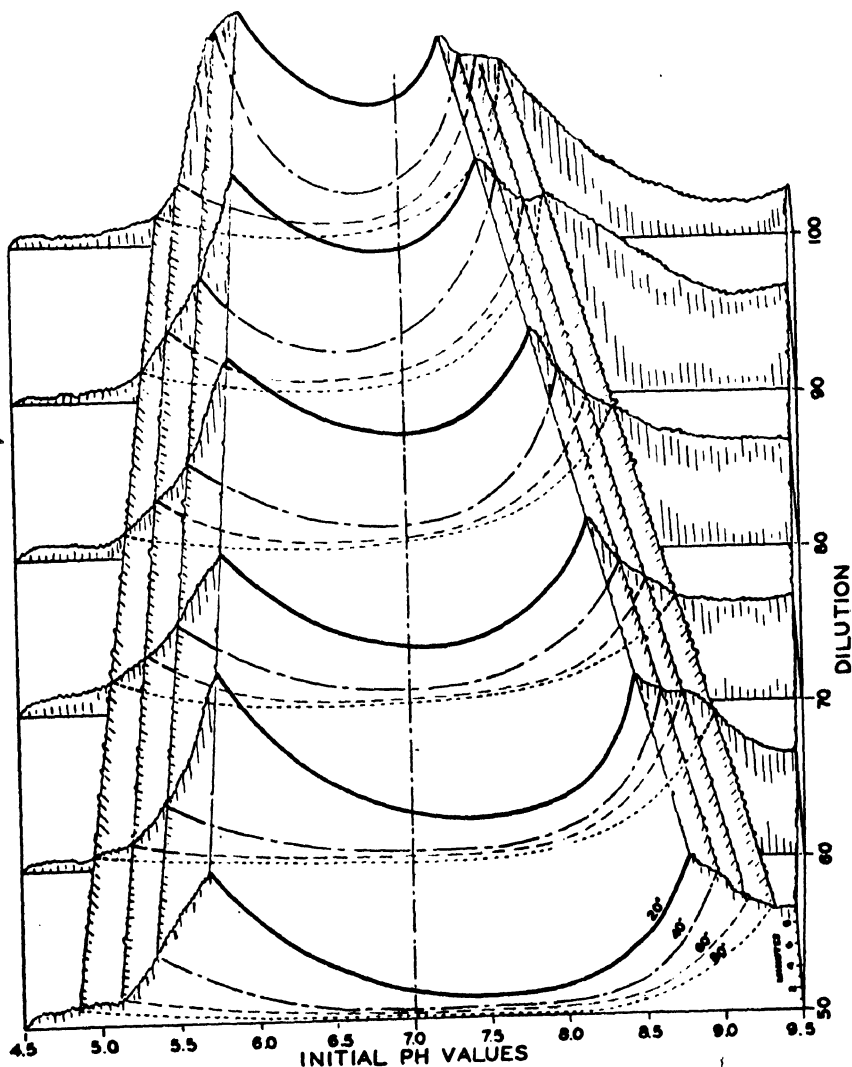


FIG. 1. Gelation time as a function of pH, dilution, and temperature

of the figure. Across the front of the unshaded base, which is indicated by the lowest horizontal line in the figure, the different initial reactions of the solutions are shown in terms of pH values. At the extreme right, along the right-hand side of the base, are given the total volumes of the

solutions in terms of milliliters; they are labeled by the rather inapt term "dilution". The least dilute solution is indicated at the front of the base by the figure "50", and the most dilute solution is indicated at the rear by the figure "100". At each dilution there rises a vertical plane upon which are plotted the data for the time interval (gelation time) elapsed before the jellies formed. It should be noted that the time scale should be imagined on the other vertical planes, each starting at zero time at the intersection of the respective vertical planes with the base. These latter intersection lines theoretically extend entirely across the figure, but for the sake of legibility are not shown in those areas where they are "hidden" by the warped surfaces. The gelation times at any single temperature, including all the pH values and dilutions at that temperature, assume the form of a concave warped surface whose intersections with the vertical planes are indicated by a series of curved lines; each temperature is indicated on the front vertical plane. The upper portions of the vertical planes and of the concave surfaces have been "torn off", and the resulting serrated edges are indicated by wavy lines. To emphasize the position of neutrality at all concentrations and temperatures, a dot-dash line has been drawn through the entire figure.

In the first complete series, the two hundred sixteen determinations were made singly. As a result of inconsistencies with the extremely alkaline and especially the extremely acid sols, thirty-eight of these determinations were repeated in duplicate. In some cases these determinations were made three or four times, each time in duplicate. Three points on the extremely acid side and one on the extremely alkaline side of the 20°C. surface were persistently inconsistent with the remaining data for that temperature. In the interest of legibility this surface was therefore idealized by slightly lowering each of these points. The figure conforms accurately to the data obtained, with these and one additional exception, that several of the lines on the extreme margins of the surfaces were extrapolated slightly beyond the actual limits at which they were determined. Except for the strongly acid and strongly alkaline sols at 60° and 80°C., whose gelation times showed a maximum error of ± 10 per cent, the maximum errors involved (2.4 to 3.5 per cent) are considered not unreasonable for this type of determination.

In some of the more concentrated solutions at least, and particularly at the higher temperatures, the data require that the conception "minimum gelation point" be expanded to what may be termed the "minimum gelation range". The mid-point of this minimum gelation range may then be compared either with the minimum gelation point of the more dilute solutions or with the minimum gelation point of the lower temperatures. Considering only the upper 20°C. surface indicated by the heavy solid lines, with attention to the lowest point of each line, it is observed that at

dilution "50" the minimum point lies near pH 7.5, at dilution "70" it lies near pH 7.0, and at dilution "100" it approaches pH 6.5. At this temperature, therefore, the minimum gelation time shifts from the alkaline, through the neutral, and toward the acid reaction as gelation takes place in progressively more dilute solutions. This relation also obtains at the higher temperatures but is less evident, since the minimum gelation time is expanded and the surfaces for the higher temperatures have not been fully extended in the acid region. This relation harmonizes several conflicting statements in the literature regarding the pH values at which gelation of silica sols takes place in minimum time. Another relation in minimum gelation time is best shown at the "100" dilution. It may be stated thus: at constant concentration, the minimum gelation time shifts from the acid reactions toward neutrality as the temperature is progressively lowered. This relation remains consistent at dilutions "80" and "90". If the conception with regard to minimum gelation range mentioned above is applied, the same tendency holds for the other dilutions. Had data been obtained at greater dilutions or lower temperatures, it is conceivable that the minimum gelation time might have shifted into the alkaline range. This assumption is supported by the data at dilution "50". This relation between minimum gelation times at constant concentration but varying temperatures appears not to have been noted previously. Parenthetically, it may be noted that the use of the minimum gelation time as an index of the position of the isoelectric point of the jellies would be questionable under the conditions obtaining in these studies.

Thus far, the use of silica jellies for bacteriological media has been necessarily confined to approximately neutral reactions since, except for the recent work by Ray and Ganguly (10), no means have been available by which jellies could be prepared at reactions deviating much from neutrality. It is evident from these data, however, that they may be prepared both at fairly acid and alkaline reactions, the range of reactions being limited by at least two factors;—concentration and temperature. The organisms studied grow less vigorously at concentrations of "50" and "60" than at greater dilutions. However, with jellies prepared at dilutions greater than "100", the bacterial colonies tend to coalesce. Accordingly, the undialyzed jellies employed for bacteriological studies in this laboratory have been employed at concentrations of "70" to "100" inclusive. In routine practice the "100" dilution has been used.

THE SHIFT IN pH VALUE DURING GELATION

Shift in pH value during gelation also limits the pH values of undialyzed jellies usable in bacteriological media. The shift has been studied as a function of concentration (dilution), initial pH value, and temperature. The technique followed was similar to that given previously. The bottles

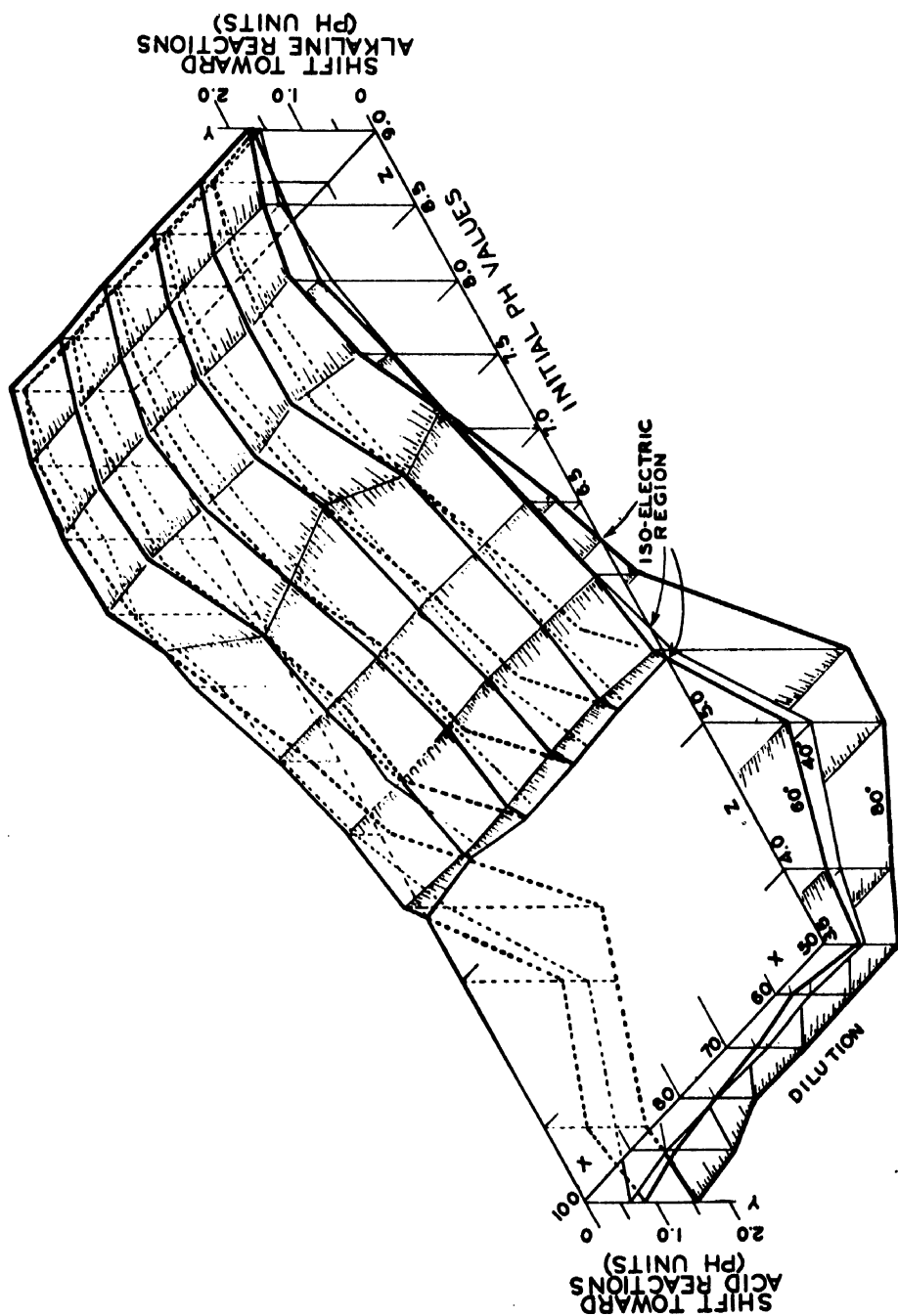


FIG. 2. Shift in pH value as a function of initial pH, dilution, and temperature

were not rotated, however, and all of the sixty-six bottles for a given temperature were placed in the water bath at one time. The temperature of the water bath was maintained at the desired point for 2 hours after the solutions were prepared and was then allowed to return to room temperature. The pH values of the sols and jellies were determined after 24 hours, again after three or four days, and finally after one week. The samples, after being stirred, were pipetted into the electrometer cup with an inverted 10-ml. pipet. Care was taken not to dilute the sample, since previous studies have shown that in strongly acid and strongly alkaline solutions even a twofold dilution may vary the reaction by as much as three-tenths of a pH unit. In strongly acid solutions the shift is toward less acid reactions, and in strongly alkaline solutions toward less alkaline reactions. The data for this study are shown graphically in figure 2. The dilutions and initial pH values are plotted along the ends and sides, respectively, of the X - Z plane. Variations in reaction from the initial pH values are plotted in terms of pH units on the Y -axis; the shifts toward more alkaline reactions are plotted above and the shifts toward more acid reactions below the X - Z plane. The shifts in pH value at any given temperature, including all the initial pH values and "dilutions" for that temperature, take the form of an S-shaped warped surface lying above the X - Z plane at neutral and alkaline reactions and below this plane at acid reactions. For the sake of legibility, the data obtained at 20°C. have not been included. Within the limits of the data, the relations found may be expressed as follows:

1. The pH values of silica sols and jellies having neutral and alkaline initial pH values shifted toward the alkaline side.
2. The pH values of slightly acid sols and jellies remained stable.
3. The pH values of more strongly acid sols and jellies shifted toward more acid reactions.
4. The shifts in pH value were greater at the higher temperatures.
5. At extremely acid and extremely alkaline initial pH values the shifts in reaction were less marked than at moderately acid and moderately alkaline reactions.
6. The shifts in pH value were largely independent of variations in concentration.
7. The shifts in pH value were independent of gel formation.
8. The positions of the hypothetical isoelectric points of these sols and jellies probably lie within the region formed by the intersections of the warped surfaces with the X - Z plane and appear to be a function of temperature.

The regions of minimum or no shift in pH value conform roughly to the region between pH values 4.64 and 5.92, in which Hurd and Griffith (4) found no shift in reaction during gelation. A similar agreement is found

with the results of Prasad and Hattiangadi (9), who found no appreciable shifts between reactions of pH 5.2 and 6.1. Had they determined the reactions of their alkaline solutions after a greater lapse of time, it is possible that the shifts in reaction which they noted would have conformed more closely to the results obtained in the study here reported. The data for the shifts in reaction from pH 7.0 are given in detail in table 2. These results agree surprisingly well with the shift in reaction (equivalent to 1.1 pH unit) which Hanks and Weintraub (3) found at initial reactions from pH 6.3 to 7.1. On the basis of this single value these authors proposed a method for preparing silica jellies at "any pH desired". In the light of the results here reported the value of the method proposed by them appears to be questionable. In connection with their work on undialyzed jellies they stated, "Observations on diluted acid-silicate mixtures suggest that the rapid pH drift does not occur until gelation is initiated; the hy-

TABLE 2
The shift in pH value from pH 7.0 toward alkaline reactions

DILUTION	TEMPERATURE			
	20°C.	40°C.	60°C.	80°C.
	<i>pH units</i>	<i>pH units</i>	<i>pH units</i>	<i>pH units</i>
50	1.22	1.10	1.19	1.02
60	1.30	1.16	1.06	1.15
70	1.31	1.08	1.37	1.20
80	1.31	1.16	1.43	1.42
90	1.31	1.19	1.42	1.15
100	1.35	1.06	1.45	1.21

drogen-ion exchange seems to be intimately related to the process of gel formation". The validity of this statement has not been verified in the present study, since shifts in pH value developed in solutions which failed to produce any evidence of gelation even after one week.

The accumulation of data which might have led to explanations of the physical-chemical factors involved in these studies was beyond the scope of the project under investigation. For this reason the author is content to follow McBain's advice (8) "... the phenomena of colloidal behavior should be described in terms of the directly observed facts rather than of theories or influences".

SUMMARY

1. Studies have been made of gelation times and of shifts in pH value of silica sols and jellies as functions of concentration, initial pH value, and

temperature. The data are expressed in the form of three-dimensional figures.

2. The data permit a reconciliation of a number of conflicting statements in the literature regarding the influence of the factors mentioned.

3. Minimum gelation time at constant concentration but at progressively lower temperatures appears to shift from acid through neutral and toward alkaline reactions.

4. Several relations have been pointed out between the factors studied and the shift in hydrogen-ion concentration of silica sols during gelation.

It is a pleasure to acknowledge the author's indebtedness to Professor R. M. Salter and Mr. C. J. Schollenberger for their interest and criticisms of the manuscript and to Dr. A. A. Hendrickson, Albert Dickinson Fellow in Soil Biology, for his assistance during the preliminary work in these studies.

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EQUILIBRIA IN THE SYSTEM POTASSIUM SULFATE-MAGNESIUM SULFATE-CALCIUM SULFATE-WATER AT 100°C.¹

J. E. CONLEY,² ALTON GABRIEL,³ AND EVERETT P. PARTRIDGE⁴

Bureau of Mines, Eastern Experiment Station, College Park, Maryland

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Among the processes proposed for the recovery of potassium sulfate from polyhalite is the extraction of the calcined complex salt with hot water. Since better results have been attained at 100°C. than at lower temperatures (4), a knowledge of the equilibria, both stable and metastable, in the system potassium sulfate-magnesium sulfate-calcium sulfate-water at this temperature is essential to an adequate understanding of the phenomena observed during these extractions. The information available concerning this four-component system is, however, fragmentary. From the data of Geiger (6) and van't Hoff (13) it has been possible to obtain an idea of the phase diagram at 83°C., and largely from the work of van Klooster (12), Basch (2), and van't Hoff a fairly complete picture of the system at 25°C. may be visualized. Data at intermediate temperatures and at temperatures above 83°C. are entirely lacking for the four-component system, although the three-component systems potassium sulfate-calcium sulfate-water and potassium sulfate-magnesium sulfate-water have been thoroughly studied at 100°C. by Hill (8) and by Starrs and Clarke (11), respectively. The present paper describes a detailed study of part of the four-component system at 100°C.

The portion of the four-component system with special bearing on the extraction of calcined polyhalite is that involving the solid phases, polyhalite ($K_2SO_4 \cdot MgSO_4 \cdot 2CaSO_4 \cdot 2H_2O$), syngenite ($K_2SO_4 \cdot CaSO_4 \cdot H_2O$), pentasalt ($K_2SO_4 \cdot 5CaSO_4 \cdot H_2O$), anhydrite ($CaSO_4$), gypsum ($CaSO_4 \cdot 2H_2O$), and hemihydrate ($CaSO_4 \cdot 0.5H_2O$). Gypsum and hemihydrate

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² Associate chemical engineer, Bureau of Mines Eastern Experiment Station, College Park, Maryland.

³ Associate chemist-petrographer, Bureau of Mines Eastern Experiment Station, College Park, Maryland.

⁴ Formerly supervising engineer, Bureau of Mines Non-metallic Experiment Station, New Brunswick, New Jersey. Now with Hall Laboratories, Inc., Pittsburgh, Pennsylvania.

appear only as metastable solid phases which are in process of replacement by anhydrite, which is the stable form of calcium sulfate at 100°C.

The concentrations of the liquid phases covered in these studies were from 0 to 17.0 g. of potassium sulfate per 100 grams of water and from 0 to approximately 14.0 g. of magnesium sulfate per 100 grams of water. This range is sufficient to include all compositions of extract solutions that are likely to be obtained by the extraction of calcined polyhalite with water at 100°C.

The investigation has included not only the stable but also some of the more frequent metastable relations through which the system passed in attaining final equilibrium. From the standpoint of the chemical engineer these metastable equilibria are of the greatest importance, especially since the stable equilibria which involve pentasalt or anhydrite as a solid phase are approached only at an extremely slow rate at 100°C. This slow establishment of equilibrium with anhydrite was noted at temperatures below 100°C. by D'Ans (5), who concluded that the difference in calcium sulfate concentration between equilibria involving gypsum and anhydrite, respectively, would not be important. That this difference in calcium sulfate has a profound effect upon the system is shown by the work reported in the present paper.

Even where a form of calcium sulfate is not involved as a solid phase, the rate of approach to equilibrium in the system is in general very slow, owing to the fact that in the decomposition of one double salt and the formation of another, all of the calcium sulfate must pass through the solution phase where the concentration is of the order of 0.2 g. of calcium sulfate per 100 grams of water.

Particular emphasis has been given to the location of the isothermally invariant polyhalite-syngenite-pentasalt and polyhalite pentasalt-anhydrite equilibria. A few experiments have been made in an effort to locate the pentasalt-syngenite and pentasalt-anhydrite invariant points in the system potassium sulfate-calcium sulfate-water at 100°C. In addition to the experiments made in the search for stable equilibrium a number of shorter-time tests in which metastable conditions were encountered have been made by taking samples of the reaction mixtures at relatively short intervals. In the study of both stable and metastable equilibria the progress of the reaction has been followed by the change in the composition of liquid phase as determined by chemical analyses and the change in the nature of the solid phases as disclosed by examination with the petrographic microscope. The attainment of stable equilibrium has been seriously retarded in many instances, owing to the inability of the natural anhydrite to enter into the reaction. In certain instances supersaturation of the liquid phase with calcium sulfate as a result of the decomposition of polyhalite and pentasalt effectively prevents any dissolution of the

anhydrite. Also, the limited solubility of anhydrite, even under favorable conditions, and a well-known slow rate of solution are contributing factors.

The metastable equilibrium studies conducted in this system consisted of time-concentration extractions of certain solid phases by means of solutions in contact with which these solid phases were not stable. These tests comprise a time-concentration extraction of polyhalite from an initial point in the pentasalt stability field, the decomposition of polyhalite by magnesium sulfate solutions in the anhydrite field, and the addition of gypsum to solutions in the stable pentasalt and polyhalite fields. The latter tests were made in an attempt to fix the limits of metastable pentasalt-gypsum equilibrium and to follow the changes occurring as the gypsum, which appeared as a decomposition product, was slowly transformed to the stable form, anhydrite. One unsuccessful attempt was made to realize the metastable invariant point for pentasalt, gypsum, and polyhalite at 100°C .

EXPERIMENTAL PROCEDURE

Long-time tests

The first experiments represented an attempt to attain the polyhalite-syngenite-pentasalt invariant point. The preliminary time-concentration tests starting with the necessary liquid and solid phases indicated that the rate of approach to equilibrium was extremely slow. It was soon realized that the mixtures would require days instead of hours to accomplish the necessary changes. Accordingly, provision was made to permit the reactions to proceed for a number of days at a carefully controlled temperature. Agitation was accomplished by attaching a number of the tubes to circular brass discs rotated vertically within the bath to impart an end-over-end motion to the tube and contents. Crisco was used as the heating bath. Temperature was automatically maintained at $100^\circ\text{C} \pm 0.2^\circ$ by a mercury-in-glass thermoregulator.

The method of placing the charges in the bath was as follows: The Pyrex tubes of sufficient size to hold 110 to 115 g. of solution, together with about 20 to 30 g. of solid material, were provided with a smaller tube for sealing and after being attached to the circular vertical disc were lowered into the Crisco bath. After the tubes had attained the temperature of the bath the desired weights of the mixture of the solid phases were introduced. The liquid phase was then heated to boiling in a small Erlenmeyer flask provided with a reflux condenser. When sufficiently hot, the solution was quickly poured into the tube and onto the solid mixture. Usually from 10 to 15 cc. of vapor space remained after the charge had been added. The small inlet tube was then quickly sealed off with an oxygen-gas torch. As soon as all tubes had been sealed the disc and tubes were turned over by hand and care taken to see that none

of the solids remained caked on the bottoms of the sample tubes. Mechanical agitation was then begun and continued as long as the samples remained in the bath. This time ranged from 15 to 50 days, 30 days being the most commonly selected time.

Considerable care was exercised in opening the tubes at the end of each experiment. The sealed tips were broken with a pair of pliers and a sampling tube consisting of a bent glass tube inserted through the straight run of a glass T-tube was attached to the reaction bulb by means of a rubber connection. Pressure applied to the horizontal outlet of the tube by the use of a rubber aspirator bulb forced the solution out of the tube onto a rapid filter paper. A few of the samples were filtered through a small cotton plug placed on the end of the glass tube used for removal of the sample. This scheme was tried both with and without the addition of a coarse filter paper around the cotton plug, and was discarded in favor of the outside rapid filter. The clear filtrate was caught in a tared glass-stoppered bottle and reserved for chemical analysis. An attempt was usually made to collect samples ranging from 50 to 60 cc. The remainder of the mixture was then thrown upon a suction filter after the tube had been removed from the bath. The solid residue was always washed, first with 95 per cent ethyl alcohol diluted with an equal volume of water, then with a small amount of 95 per cent alcohol. The washed residue was then air-dried and reserved for microscopic examination.

The solutions were analyzed for potassium by the modified chloroplatinate method of Hicks (7). The calcium content was obtained by separation in small volume as the oxalate with a double precipitation, and after solution in dilute sulfuric acid was determined volumetrically by titration with $N/50$ or $N/100$ standard permanganate, depending upon the size of sample used. After separation of the calcium oxalate, the magnesium was precipitated as magnesium ammonium phosphate and weighed as pyrophosphate after ignition. The equivalent sulfate was then calculated for each constituent.

Time-concentration studies

While in many cases metastable equilibrium was encountered in mixtures in the sealed tubes agitated in the thermostat, a different technique was generally used on the short-time tests involving metastable conditions. The apparatus used in the latter tests consisted of a three-necked Pyrex flask provided with a reflux condenser, a sampling outlet tube, and a mechanical stirring device. Heating was accomplished by means of an electric heater. Mixtures containing from 750 to 800 g. of water were commonly used with varying amounts of solid phases. In general, the quantity of solids added was limited to the amount that could be readily kept in suspension. In certain instances, large amounts were necessary

to attain the proper concentration changes desired. Samples of the liquid phases were obtained by applying pressure to the top of the reflux condenser so as to force a portion onto a rapid filter. The filtered and tared samples were analyzed as previously indicated, and the solid residues remaining on the filter paper were washed with 1:1 alcohol-water and 95 per cent alcohol, and then air-dried.

Materials used

Only materials of selected purity were used in preparing the mixtures of liquid and solid phases. Baker's c.p. chemicals of tested purity were

TABLE 1
Composition of synthetic solid phases used

LOT NO.	COMPOSITION		
	K_2SO_4	MgSO_4	CaSO_4
	per cent	per cent	per cent
Syngenite ($\text{K}_2\text{SO}_4 \cdot \text{CaSO}_4 \cdot \text{H}_2\text{O}$)			
Theoretical.....	53.07		41.45
P16.....	52.78		
P17.....	51.85		
P18.....	51.98	Nil	41.70
P20.....	52.35	Nil	42.70
Pentasalt ($\text{K}_2\text{SO}_4 \cdot 5\text{CaSO}_4 \cdot \text{H}_2\text{O}$)			
Theoretical.....	19.96		77.98
P19.....	18.99	Nil	77.97
P30.....	21.08	Nil	77.44
Polyhalite ($\text{K}_2\text{SO}_4 \cdot \text{MgSO}_4 \cdot 2\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$)			
Theoretical.....	28.9	20.00	45.10
P21.....	29.48	19.17	45.81
P31.....	29.53	19.30	46.07

used as the source of the dehydrated calcium sulfate and the potassium and magnesium sulfates.

The natural anhydrite used was a sample of high purity obtained from Midland, California. This product was ground to minus 100-mesh and later to a much finer size by pulverizing in a pebble mill for several days. The finer material was used in all experiments involving anhydrite except experiment 8.

The double salts—pentasalt, syngenite, and polyhalite—were prepared from gypsum and solutions of potassium and magnesium sulfates by the usual methods, which consisted of choosing a solution composition and temperature for the reaction definitely known from available literature or from previous experience to be in the stable field for the synthesis of the desired solid phase. For instance, room temperatures were used for prep-

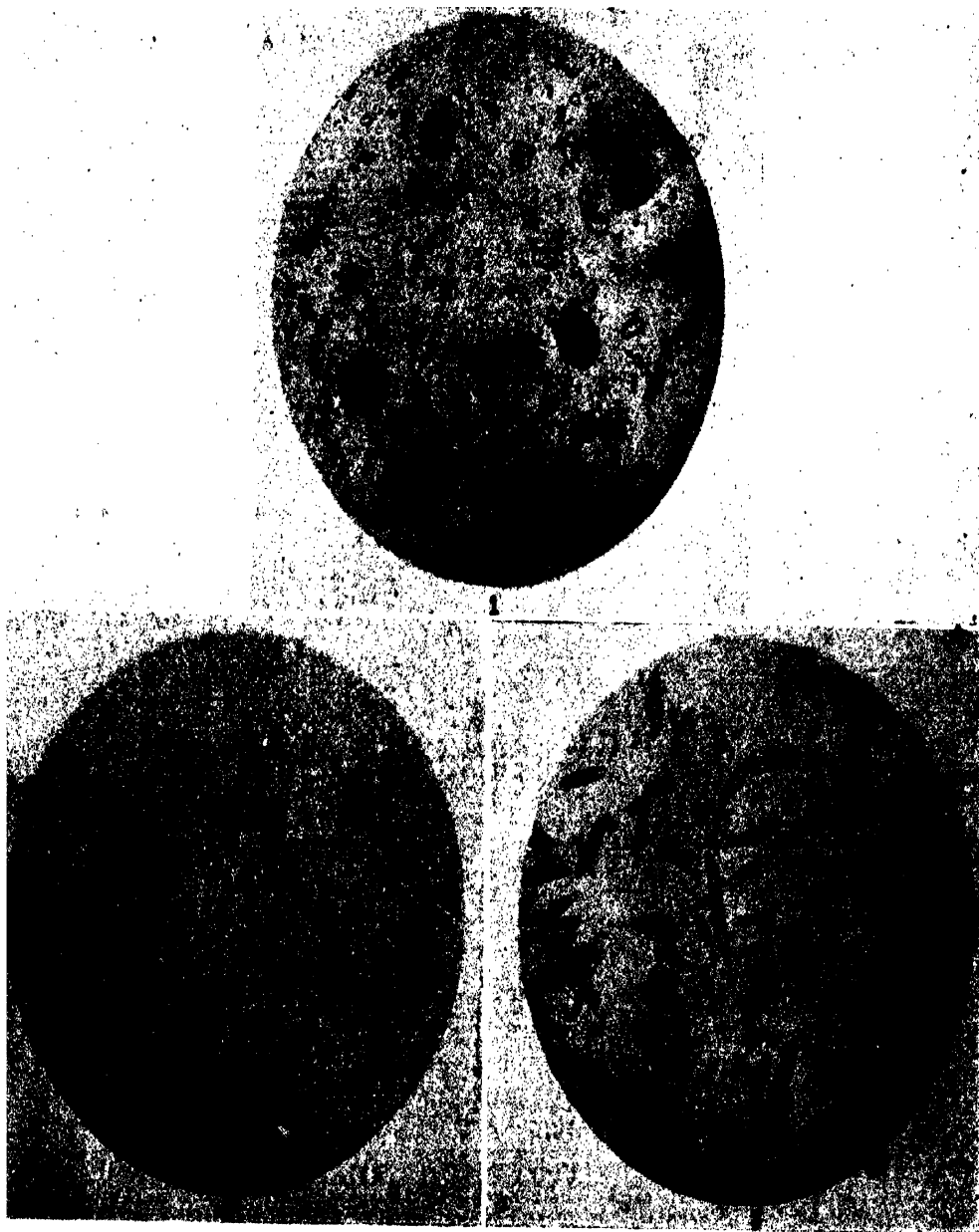


FIG. 1. Photomicrographs of double salts encountered in the system potassium sulfate-magnesium sulfate-calcium sulfate-water. (1) Polyhalite, $K_2SO_4 \cdot MgSO_4 \cdot 2CaSO_4 \cdot 2H_2O$, $\times 75$. (2) Syngenite, $K_2SO_4 \cdot CaSO_4 \cdot H_2O$, $\times 75$. (3) Pentasalt, $K_2SO_4 \cdot 5CaSO_4 \cdot H_2O$, $\times 75$.

aration of syngenite and the temperatures of the boiling solutions for pentasalt and polyhalite. The reacting mixtures were agitated by mechanical stirrers, and in the case of the higher temperatures were heated under reflux condensers. The double salts were refined by filtering from the first solution and treating with fresh solutions of either potassium sulfate or potassium sulfate and magnesium sulfate, depending upon whether syngenite and pentasalt or polyhalite were being produced. Any excess of gypsum, which was the form of calcium sulfate used, was eliminated by the refining treatment. The earlier lots of these synthetic salts were subjected to chemical analysis and also examined under the petrographic microscope. Typical analyses of some of the products used are given in table 1. Figure 1 illustrates the distinctive crystal habits of the double salts, which served as a guide in microscopic examination, although identification was always based on actual measurement of optical properties.

EXPERIMENTAL RESULTS

As previously indicated, the usual procedure in the studies aimed at the determination of stable equilibrium was to seal a mixture of the necessary liquid and solid phases in a Pyrex tube and to agitate the charge within a thermostat for periods of 20 to 40 days. A few of the samples in the first experiments, in which only occasional manual agitation was used, were held in the bath for 69 days.

The usual practice was to add two solid phases to the mixture when it was desired to secure a point in the equilibrium diagram on the boundary line between these two solid phases. These equilibria of course are isothermally univariant with respect to the four-component system potassium sulfate-magnesium sulfate-calcium sulfate-water and isothermally univariant with respect to the three-component system potassium sulfate-calcium sulfate-water. When it was desired to approach the invariant points in the four-component system, that is, equilibria involving three solid phases, all three solid phases were added to the initial reaction mixture. The extremely slow rate of decomposition of many of the solid phases containing calcium sulfate very seriously handicapped the attainment of equilibrium conditions in a reasonable time. For this reason, initial starting mixtures were usually selected so as to take advantage of the more active reaction rates of certain solid phases. This plan partly explains the comparatively large number of mixtures originally started with a solution phase corresponding to concentrations in the polyhalite field.

Methods of representation

A space model is desirable in the interpretation of the data for the four-component system. It is possible, however, to analyze the results

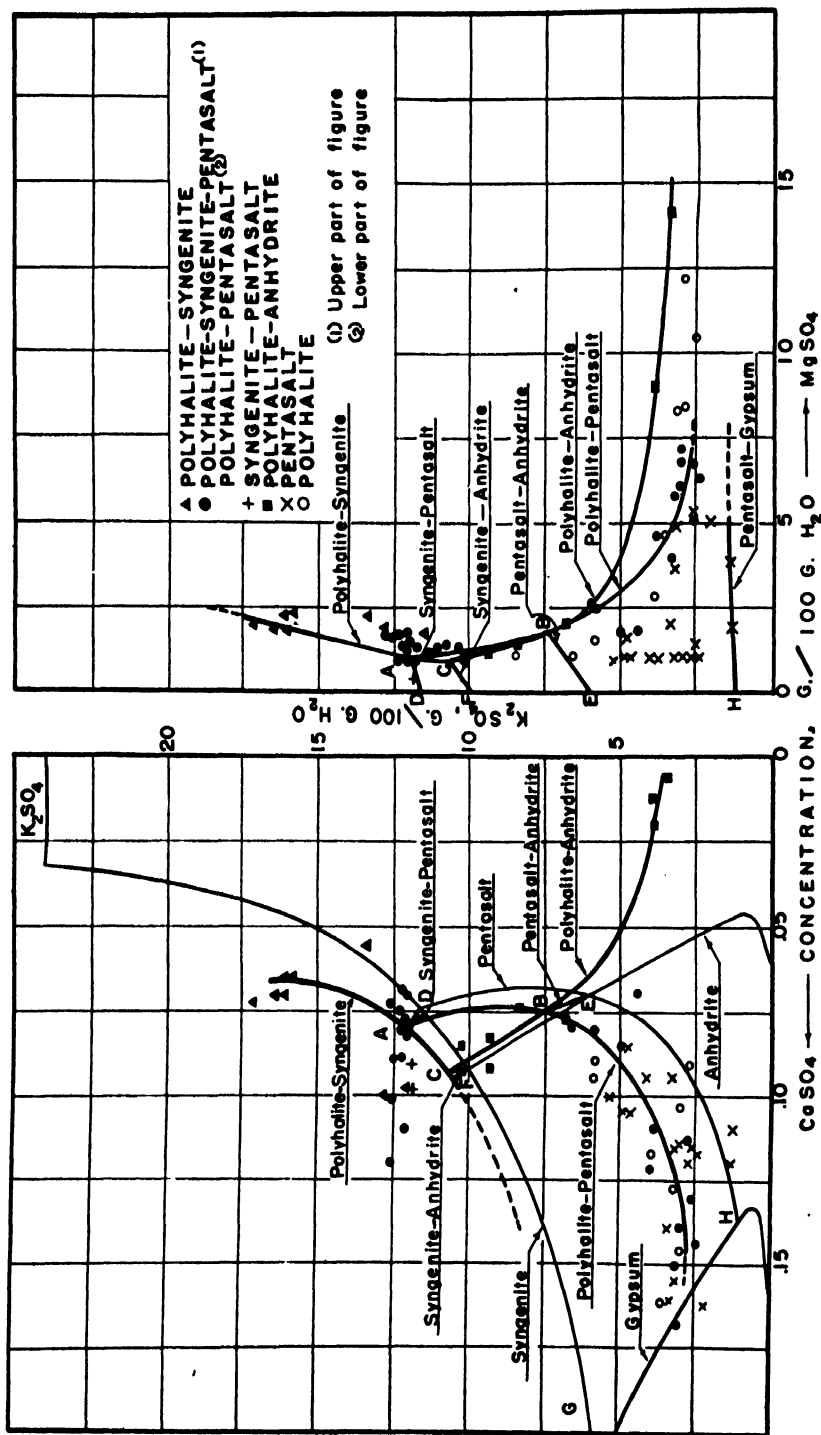


FIG. 2. Plot of experimental data in the system potassium sulfate-magnesium sulfate-calcium sulfate-water at 100°C, on potassium sulfate-calcium sulfate and potassium sulfate-magnesium sulfate planes.

in terms of projections on the potassium sulfate-calcium sulfate, calcium sulfate-magnesium sulfate, and potassium sulfate-magnesium sulfate planes. Figures 2 to 5, inclusive, show the experimental values in this manner. Figure 6 represents a projection of the space model, the positions of the various equilibria being derived from the preceding figures.

Polyhalite-syngenite boundary line

The experiments to determine the location of the syngenite-polyhalite boundary line up to approximately 17.0 g. of potassium sulfate per 100 grams of water are shown in table 2 and represented graphically in figures 2 and 3. Table 2 gives the results obtained in several experiments by adding a mixture of syngenite and polyhalite to a solution of potassium

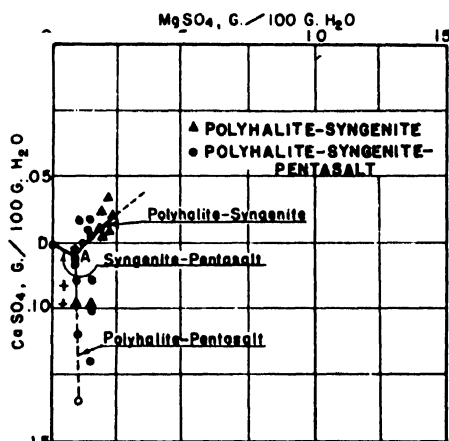
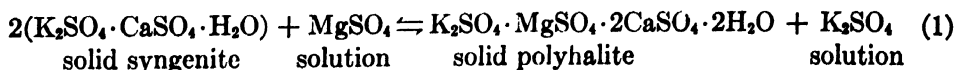


FIG. 3. Plot of experimental data on magnesium sulfate-calcium sulfate plane to determine the polyhalite-syngenite boundary line at 100°C.

and magnesium sulfates and allowing the reaction to proceed for 19, 27, or 30 days as indicated in the specific instances. All of these samples, except No. 7, showed a decrease in magnesium sulfate and an increase in potassium sulfate. This change indicates the formation of a solid phase containing magnesium sulfate and the decomposition of an original solid containing potassium sulfate. Examination by the microscope showed the syngenite to be badly corroded with well-formed polyhalite appearing from solution. These facts, together with additional data to be presented later, permit tentative location of the syngenite-polyhalite boundary line. This represents a considerable change from the line determined by Geiger (6) and van't Hoff (13) at 83°C. The chemical reaction involved in these tests is as follows:



Obviously the reaction proceeds from left to right when syngenite is decomposing in the polyhalite field, and in the reverse direction when polyhalite is decomposing in the syngenite field.

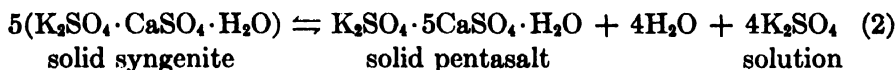
TABLE 2
*Equilibrium in the system K_2SO_4 - $MgSO_4$ - $CaSO_4$ - H_2O at $100^\circ C$.
Syngenite-polyhalite boundary line*

SAMPLE NO.	TIME IN THER- MOSTAT	PROPORTIONS OF ORIGINAL MIXTURE						CONCENTRATION OF LIQUID PHASE IN GRAMS PER 100 GRAMS OF WATER					PETROGRAPHIC DATA ON SOLIDS	
		Weight of solids		Weight of solution components			Initial		Final			F = Forming D = Dissolving		
		P.H.*	S.†	K ₂ SO ₄	MgSO ₄	H ₂ O	K ₂ SO ₄	MgSO ₄	K ₂ SO ₄	MgSO ₄	CaSO ₄	P.H.	S.	
		grams	grams	grams	grams	grams	grams	grams	grams	grams	grams			
1	27	1.0	15.0	9.22	4.61	82.2	11.1	2.8	12.84	1.59	0.100	F	D	
2	19	2.0	15.0	9.70	2.7	77.5	12.5	3.5	13.45	2.17	0.058	F	D	
3	30	10.0	10.0	14.0	3.0	100.0	14.0	3.0	15.79	2.26	0.066	F	D	
4	19	20.0	2.0	9.75	1.3	65.0	15.0	2.0	16.03	1.76	0.065	D	F	
5	30	10.0	10.0	15.10	2.5	99.9	15.0	2.5	16.07	2.19	0.071	F	D	
6	30	10.0	10.0	15.99	2.0	100.1	16.0	2.0	16.55	1.96	0.071	F	D	
7	30	10.0	10.0	17.0	1.5	100.0	17.0	1.5	17.15	1.88	0.073	F	D	
8	27	15.0	1.0	15.1	1.0	99.7	15.0	1.0	12.11	0.99	0.098	D	F	

* P.H. = polyhalite. † S. = syngenite.

Syngenite-pentasalt equilibria

The few tests made to determine a point on the pentasalt-syngenite boundary line are given in table 3. Owing to the apparent shortness of this line only a limited number of tests were deemed necessary. The results obtained on samples 17 and 18 represent duplicate runs in every respect except for the time during which the mixture was allowed to react. The final concentrations attained in both these experiments were practically identical. The reaction involved in these tests is as follows:



The reaction is from left to right when syngenite is decomposing in the pentasalt field, and from right to left when pentasalt is decomposing in the syngenite stability region.

Several experiments were made to determine the pentasalt-syngenite invariant point in the three-component system at $100^\circ C$. These data are given in table 3 and also plotted in figures 2 and 3. Syngenite was added to potassium sulfate solutions of various concentrations considered to be below the invariant point, and pentasalt was added to solutions of concentrations higher than that point. The chemical reactions are the same as

given by equation 2. Some of the tests, as illustrated by samples 10 and 12, showed little, if any, change even in 69 days. Later tests based upon the decomposition of syngenite yielded larger changes. The values secured on samples 12, 14, 15, and 16 are believed to represent the best results. The average of these four figures corresponds to 11.7 g. of potassium sulfate and 0.075 g. of calcium sulfate per 100 grams of water as the equilibrium point. This value, which is higher than the corresponding point for 83°C. as determined by van't Hoff and Geiger, and also higher than the figure 8.7 g. of potassium sulfate per 100 grams of water proposed for 100°C. by Anderson and Nestell (1), checks closely the results of Hill (8) at the

TABLE 3
Equilibrium in the system K_2SO_4 - $MgSO_4$ - $CaSO_4$ - H_2O at 100°C.
Syngenite-pentasalt boundary line

SAMPLE NO.	TIME IN THER- MOSTAT	PROPORTIONS OF ORIGINAL MIXTURE					CONCENTRATION OF LIQUID PHASE, IN GRAMS PER 100 GRAMS OF WATER					PETROGRAPHIC DATA ON SOLIDS	
		Weight of solids		Weight of solution components			Initial			Final		F = Forming D = Dissolving	
		P.S.*	S.†	K_2SO_4	$MgSO_4$	H_2O	K_2SO_4	$MgSO_4$	K_2SO_4	$MgSO_4$	$CaSO_4$	P.S.	S
	days	grams	grams	grams	grams	grams	grams	grams	grams	grams	grams		
9	40	2.5	2.5	2.85	0	25	11.42	0	11.41	0		F	D
10	69	2.5	2.5	2.85	0	25	11.42	0	11.48	0			
11	40	5.0	0	3.0	0	25	12.04	0	12.03	0			
12	69	5.0	0	3.0	0	25	12.04	0	11.84	0			
13	40	0	5.0	2.7	0	25	10.80	0	11.20	0			
14	69	0	5.0	2.7	0	25	10.80	0	11.77	0			
15	18	12.0	8.0	10.38	0	83.0	12.50	0	11.67	0	0.075	D	F
16	18	8.0	12.0	8.74	0	76.0	11.50	0	11.52	0	0.075	F	D
17	20	10.0	15.0	9.89	0.45	89.0	11.0	0.50	12.00	0.46	0.098	F	D
18	26	10.0	15.0	9.80	0.45	88.2	11.0	0.50	12.01	0.47	0.091	F	D

* P.S. = pentasalt. † S. = syngenite.

latter temperature. Additional investigation by Clarke and Partridge (3) at more elevated temperatures would also tend to substantiate the higher concentrations found in the present work. In the light of the decided tendency for metastable equilibrium and the relatively short reaction periods used by the earlier investigators, it is likely that they failed to reach stable equilibrium.

Polyhalite-pentasalt-syngenite invariant point at 100°C.

A considerable number of reaction mixtures of varying initial compositions have been used to determine the equilibrium point at which syngenite, pentasalt, and polyhalite may coexist at 100°C. This point has been ap-

proached from initial starting compositions in both the polyhalite and the syngenite stability fields. Many of the tests indicated that pentasalt can exist as a metastable phase for prolonged periods, so that only a few experiments have been made in which the decomposition of pentasalt was expected to effect relatively large changes. The data on the various samples used, including information on the proportions of the solid phases

TABLE 4
Equilibrium in the system K_2SO_4 - $MgSO_4$ - $CaSO_4$ - H_2O at $100^\circ C$.
Polyhalite-pentasalt-syngenite invariant point

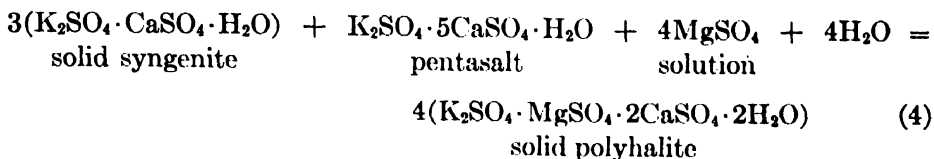
SAMPLE NO.	TIME IN THERMOSTAT	PROPORTIONS OF ORIGINAL MIXTURE						CONCENTRATION OF LIQUID PHASE, IN GRAMS PER 100 GRAMS OF WATER					PETROGRAPHIC DATA ON SOLIDS		
		Weight of solids			Weight of solution components			Initial		Final			F = Forming D = Dissolving U = Unaltered		
		P.H.*	P.S.†	S.‡	K_2SO_4	$MgSO_4$	H_2O	K_2SO_4	$MgSO_4$	K_2SO_4	$MgSO_4$	$CaSO_4$	P.H.	P.S.	S.
	days	gms.	gms.	grams	grams	gms.	grams	grams	gms.	grams	gms.	grams			
19	40	1.0	2.5	2.5	2.23	0.64	25.0	8.92	2.56	11.80	1.36				
20	69	1.0	2.5	2.5	2.23	0.64	25.0	8.92	2.56	12.17	1.20				
21	40	1.0	2.5	2.5	2.23	0.64	25.0	8.92	2.56	11.78	1.27				
22	69	1.0	2.5	2.5	2.23	0.64	25.0	8.92	2.56	12.06	1.11				
23	45	10.0	10.0	10.0	14.65	2.40	142.95	10.25	1.68	12.10	0.110				
24	20	10.5	15.0	9.0	9.65	0.37	73.4	13.14	0.50	12.25	0.94	0.089	D	D	F
25	26	7.0	10.0	6.0	13.00	0.50	99.45	13.10	0.50	12.24	0.94	0.089	D	D	F
26	19	1.5	9.0	10.0	13.00	2.00	101.1	12.86	1.98	12.49	1.61	0.089	F	D	D
27	27	1.5	9.0	10.0	13.00	2.00	101.1	12.86	1.98	12.61	1.56	0.120	F	D	D
28	19	1.5	7.5	12.0	10.74	1.80	91.3	11.76	1.98	12.54	1.59	0.101	F	U	D
29	26	1.5	7.5	12.0	12.00	2.00	101.1	11.87	1.98	12.58	1.57	0.073	F	F(?)	D
30	10	8.0	8.0	8.0	10.65	0.90	88.0	12.10	1.00	11.90	0.91	0.082	D	D	F
31	19	8.0	8.0	8.0	9.98	0.82	82.5	12.10	1.00	11.86	0.89	0.080	D	D	F
32	10	8.0	8.0	8.0	10.71	1.28	85.0	12.60	1.50	12.21	1.23	0.075	U	D	F
33	19	8.0	8.0	8.0	11.09	1.32	88.0	12.60	1.50	12.13	1.20	0.069	U	D	D
34	10	5.0	8.0	12.0	11.10	1.93	96.5	11.50	2.00	12.08	1.52	0.069	F	F	D
35	19	5.0	8.0	12.0	10.64	1.85	92.5	11.50	2.00	12.10	1.42	0.070	F	D	D
36	10	12.0	8.0	5.0	11.83	0.90	91.0	13.00	1.00	11.96	0.93	0.081	F	F	D
37	19	12.0	8.0	5.0	11.05	0.85	85.0	13.00	1.00	12.09	0.92	0.078	D	D	F

* P.H. = polyhalite. † P.S. = pentasalt. ‡ S. = syngenite.

added to the initial starting solution, the initial and final compositions of the liquid phases, and data on the solid phases from microscopic examination are given in table 4. These data are also represented graphically in figures 2 and 3.

Reference to the tabulated results will show that all three solid phases (polyhalite, pentasalt, and syngenite) were added to the initial mixtures.

As most of these samples were originally in the polyhalite field, a smaller proportion of that salt was usually present in the sample. Obviously the chemical reactions representing the changes occurring when pentasalt and syngenite are present as unstable phases in the polyhalite field may be represented by the following equation:



The paths of liquid-phase changes would therefore depend upon the relative rates of decomposition of the two unstable phases. The net changes attained in the various samples definitely indicate a rapid rate of decomposition for syngenite, with a much slower rate for pentasalt. In fact, it may be shown by stoichiometric calculations based on concentration changes and also by microscopic data that the greater portion of the total changes was due to the decomposition of the syngenite with simultaneous conversion to polyhalite. Similarly pentasalt is fairly stable in the syngenite field, while polyhalite decomposes to form syngenite at a much more rapid rate. This latter condition would require the reaction as indicated by equation 4 to proceed from right to left.

It may be seen from the data in table 4 and figures 2 and 3 that many of the reaction mixtures had failed to reach equilibrium in the allotted time, although the solution composition changes were tending to approach the desired point. The average of the ten samples comprising tests 20, 22, 23, 24, 25, 28, 30, 31, 32, and 33 yields values of 12.10 g. of potassium sulfate, 1.05 g. of magnesium sulfate, and 0.084 g. of calcium sulfate per 100 grams of water. However, from inspection of figures 2 and 3, samples 30, 31, 36 and 37 are believed to represent the best approach to equilibrium, which has accordingly been taken as 12.1 g. of potassium sulfate, 0.9 g. of magnesium sulfate, and 0.08 g. of calcium sulfate per 100 grams of water. It seems quite possible that the higher values for magnesium sulfate may represent points in the polyhalite surface not yet in equilibrium with the other solid phases.

Polyhalite-pentasalt boundary line

Data obtained in the experiments made to determine the polyhalite-pentasalt boundary line at 100°C. are presented in table 5 and plotted in figures 2 and 4. Since pentasalt was found to persist as a metastable form, under some conditions, for as long as 60 days, attempts made to approach the line from points in the polyhalite stability region had but slight success. Polyhalite was found to decompose fairly readily to pro-

duce pentasalt, but pentasalt was converted to polyhalite at an extremely slow rate.

TABLE 5
Equilibrium in the system K_2SO_4 - $MgSO_4$ - $CaSO_4$ - H_2O at $100^\circ C$.
Polyhalite-pentasalt boundary line

SAMPLE NO.	TIME IN THERMOSTAT	PROPORTIONS OF ORIGINAL MIXTURE						CONCENTRATION OF LIQUID PHASE, IN GRAMS PER 100 GRAMS OF WATER					PETROGRAPHIC DATA ON SOLIDS		
		Weight of solids			Weight of solution components			Initial		Final			F = Forming D = Dissolving U = Unaltered		
		P.H.*	P.S.†	S.‡ or A.§	K_2SO_4	$MgSO_4$	H_2O	K_2SO_4	$MgSO_4$	K_2SO_4	$MgSO_4$	$CaSO_4$	P.H.	P.S.	A.
	days	gms.	gms.	grams	gms.	gms.	grams	gms.	gms.	grams	gms.	grams			
38	40	2.0	2.0	2.0	2.08	0.53	25.0	8.30	2.10	11.14	1.32				
39	69	2.0	2.0	2.0	2.08	0.53	25.0	8.30	2.10	11.04	1.25				
40	40	2.0	2.0	2.0	2.08	0.53	25.0	8.30	2.10	11.06	1.22				
41	69	2.0	2.0	2.0	2.08	0.53	25.0	8.30	2.10	10.94	1.15				
42	40	1.0	2.5	2.5	1.93	0.61	25.0	7.72	2.53	10.93	1.43				
43	69	1.0	2.5	2.5	1.93	0.61	25.0	7.72	2.53	10.84	1.35				
44	40	2.5	2.5	1.0	2.21	0.39	25.0	8.83	1.54	10.43	1.30				
45	69	2.5	2.5	1.0	2.21	0.39	25.0	8.83	1.54	10.39	1.26				
46	40	2.5	2.5	1.0	2.21	0.39	25.0	8.83	1.54	10.34	1.23				
47	69	2.5	2.5	1.0	2.21	0.39	25.0	8.83	1.54	10.30	1.17				
48	40	2.5	1.0	2.5	1.91	0.38	25.0	7.64	1.53	11.32	1.13				
49	69	2.5	1.0	2.5	1.91	0.38	25.0	7.64	1.53	11.51	1.06				
50	40	2.5	1.0	2.5	1.91	0.38	25.0	7.64	1.53	11.37	1.09				
51	69	2.5	1.0	2.5	1.91	0.38	25.0	7.64	1.53	11.41	0.98				
52	40	1.0	15.0		4.80	2.40	80.0	6.00	3.00	5.88	2.63	0.081	F	D	
53	39	1.0	15.0		4.00	5.00	100.0	4.00	5.00	3.84	4.63	0.109	F	D	
54	40	8.0	8.0	8.0	2.45	6.37	98.0	2.50	6.50	2.73	6.47	0.113	F	D	F
55	38	5.0	10.0	10.0	1.25	4.82	63.0	2.00	8.00	3.05	6.81	0.168	D(?)	D	F
56	38	10.0	10.0	2.0	0.67	4.02	67.0	1.00	6.00	2.38	6.29	0.144	D	F(?)	F(?)
57	38	0	1.0	20.0	3.40	0.85	85.0	4.00	1.00	4.78	1.60	0.085			
58	30	10.0	10.0	0	3.32	2.90	83.0	4.00	3.50	4.00	3.26	0.122	F	D	
59	32	20.0	0	0	4.30	1.15	72.0	6.00	1.60	5.86	1.58	0.095	U		
60	33	20.0	0	0	5.67	0	81.0	7.00	0	8.43	1.06	0.134	D	F	
61	33	20.0	0	0	3.15	2.50	83.0	3.80	3.00	3.89	2.77	0.117	U		
62	30	25.0	0	0	6.30	0	90.0	7.00	0	6.62	1.10	0.080	F(?)	D(?)	
63	30	1.0	20.0	0	7.20	4.00	90.0	8.00	4.44	5.82	2.39	0.090	F	D	
64	26	18.0	1.0	15.0	4.50	1.80	90.0	5.00	2.00	4.44	1.79	0.070	D	F	D

* P.H. = polyhalite. † P.S. = pentasalt. ‡ S. = syngenite. § A. = anhydrite.

Experiments 38 to 52 were made to locate the polyhalite-pentasalt-syngenite invariant point and originally contained all three solid phases. Owing to the large change in concentrations needed to reach this point,

practically all of the syngenite present in the various samples dissolved and was replaced by polyhalite, the stable solid phase. Chemical analyses and stoichiometric calculations showed but a very small residual quantity of syngenite in the final solids in samples 38 to 46 and none in samples 47 to 51. These latter tests therefore tended to approach the polyhalite-pentasalt boundary line rather than the polyhalite-pentasalt-syngenite point.

The grouping of the several end solution concentrations fixes the directional trend of the boundary line. Tests 60 and 62 were made in an at-

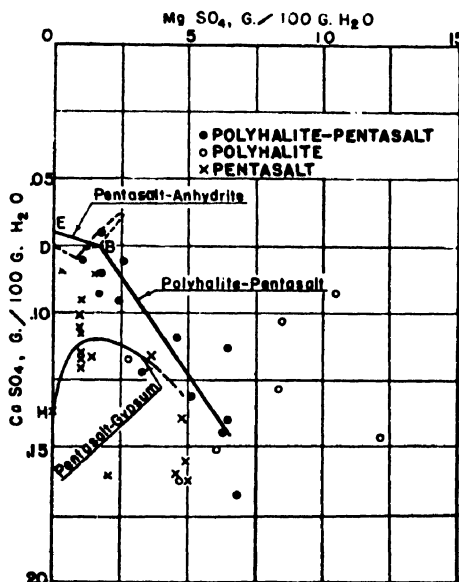


FIG. 4

FIG. 4. Plot of experimental data on magnesium sulfate-calcium sulfate plane to determine the polyhalite-pentasalt boundary line at 100°C.

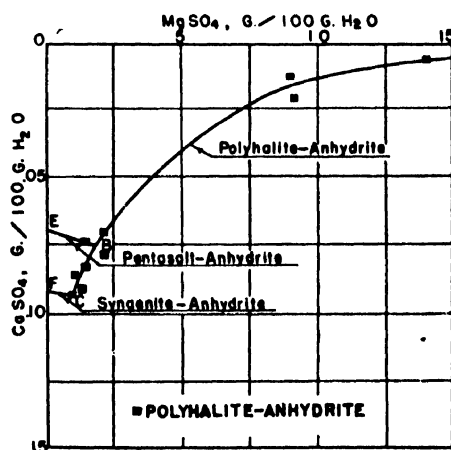


FIG. 5

FIG. 5. Plot of experimental data on magnesium sulfate-calcium sulfate plane to determine the polyhalite-anhydrite boundary line at 100°C.

tempt to reach the polyhalite-pentasalt boundary line by decomposing polyhalite by means of a solution of potassium sulfate. Well-formed pentasalt was produced, probably metastable, and the compositions of the end solutions failed to reach the boundary line as desired.

Pentasalt-anhydrite equilibria

The stable equilibria between pentasalt and anhydrite encountered in the system potassium sulfate-magnesium sulfate-calcium sulfate-water consist of the invariant point, pentasalt-anhydrite, in the magnesium sulfate-free system, and the invariant equilibria which constitute the

TABLE 6
Equilibrium in the system K_2SO_4 - $MgSO_4$ - $CaSO_4$ - H_2O at $100^\circ C$.
Pentasalt-anhydrite boundary line

SAMPLE NO.	TIME IN THERMOSTAT	PROPORTIONS OF ORIGINAL MIXTURE						CONCENTRATION OF LIQUID PHASE, IN GRAMS PER 100 GRAMS OF WATER					PETROGRAPHIC DATA ON SOLIDS		
		Weight of solids			Weight of solution components			Initial		Final			F = Forming D = Dissolving U = Unaltered		
		P.H.*	P.S.†	A.‡	K_2SO_4	$MgSO_4$	H_2O	K_2SO_4	$MgSO_4$	K_2SO_4	$MgSO_4$	$CaSO_4$	P.H.	P.S.	A.
	days	gms.	gms.	gms.	grams	grams	grams	gms.	grams	gms.	grams	grams			
53	39	1.0	15.0	0	4.0	5.0	100.0	4.00	5.00	3.84	4.63	0.109	F	D	Nil
54	40	8.0	8.0	8.0	2.45	6.37	98.0	2.50	6.50	2.73	6.47	0.113	F	D	F
55	38	5.0	10.0	10.0	1.25	4.82	63.0	2.00	8.00	3.05	6.81	0.168	D	D	F
56	38	10.0	10.0	2.0	0.67	4.02	67.0	1.00	6.00	2.38	6.29	0.144	D	F	F
58	30	10.0	10.0	0	3.32	2.90	83.0	4.00	3.50	4.00	3.26	0.122	F	D	Nil
61	33	20.0	0	0	2.74	8.43	98.0	2.80	8.50	2.96	8.45	0.103	U	Nil	Nil
64	26	18.0	1.0	15.0	4.50	1.80	90.0	5.00	2.00	4.44	1.79	0.070	D	F	D
65	40	0	8.0	12.0	2.0	1.5	100.0	2.00	1.50	2.55	1.39	0.116		D	F
66	40	0	8.0	12.0	1.8	2.7	90.0	2.00	3.00	3.13	4.17	0.124		D	F
67	40	15.0	10.0	0	1.7	4.3	85.0	2.00	5.00	2.14	5.05	0.162		D	F
68	38	0	1.0	20.0	3.4	0	85.0	4.00	0	4.16	0	0.079		D	F
69	30	0	2.0	20.0	4.15	0	69.0	6.00	0	5.60	0	0.104		F	D
70	30	0	2.0	20.0	1.98	1.32	66.0	3.00	2.00	3.35	2.05	0.161		D	F
71	32	0	15.0	0	1.64	0.82	82.0	2.00	1.00	2.40	1.06	0.117		D	F
72	32	0	15.0	0	1.97	0.82	82.0	2.40	1.00	2.72	1.06	0.120		D	F
73	32	0	15.0	0	2.04	0.73	73.0	2.80	1.00	2.98	1.06	0.114		D	F
74	32	0	15.0	0	2.53	0.79	79.0	3.20	1.00	3.29	1.07	0.095		D	F
75	32	0	15.0	0	2.92	0.81	81.0	3.60	1.00	3.78	1.03	0.107		D	F
76	32	0	15.0	0	4.00	0.99	99.0	4.00	1.00	4.12	1.05	0.095		D	F
77	32	0	15.0	0	4.09	0.93	93.0	4.40	1.00	4.70	1.01	0.105		D	F
78	32	0	15.0	0	4.80	0.99	99.0	4.80	1.00	4.90	1.06	0.105		D	F
79	32	0	20.0	0	2.58	4.60	92.0	2.80	5.00	3.18	4.91	0.155		D	F
80	33	0	0	20.0	4.48	0	80.0	5.60	0	5.67	0			U	
81	33	0	15.0	0	4.68	0.90	90.0	5.20	1.00	5.27	0.97	0.101		D	F
82	33	0	0	20.0	5.30	0.98	98.0	5.40	1.00	5.21	0.93			U	
83	33	0	15.0	0	3.06	4.50	90.0	3.40	5.00	3.46	4.77	0.139		D	F
84	29	0	25.0	0	0	0	90.0	0	0	1.08	0	0.11		D	F(?)
85	25	0	2.0	20.0	2.70	0	90.0	3.00	0	3.15	0	0.06		D	F(?)
86	29	0	25.0	0	0.90	1.80	90.0	1.00	2.00	1.24	1.79	0.11		D	Trace§
87	29	0	25.0	0	0.90	3.60	90.0	1.00	4.00	1.36	3.84	0.12		D	F
88	7	0	75.0	0			800.0	2.84	5.13	3.18	5.33			U	
89	40	10.0	10.0	2.0	3.68	0.92	92.0	4.00	1.00	4.91	1.75	0.085	D	F	D
90	40	20.0	1.0	0	1.80	2.70	90.0	2.00	3.00	3.21	3.68	0.116	D	D	F
91	40	5.0	5.0	10.0	1.53	5.85	90.0	1.70	6.50	2.97	6.42	0.139	D	D	F
92	38	15.0	10.0	0	1.20	3.00	60.0	2.00	5.00	2.61	5.13	0.131	D	F	F
93	30	2.0	0	20.0	1.74	6.96	58.0	3.00	12.00	2.88	12.15	0.146	F		D
94	30	2.0	0	20.0	1.46	7.30	73.0	2.00	10.00	2.59	10.45	0.092	D		F
95	30	8.0	8.0	8.0	2.56	6.05	93.0	2.75	6.50	3.09	6.10	0.151	D-F	D	F
96	33	20.0	0	0	3.53	4.90	98.0	3.60	5.00	3.63	4.68	0.162	D	Nil	F
97	33	0	0	20.0	2.86	7.56	84.0	3.40	9.00	3.18	8.29	0.128	Nil	Nil	U
98	33	20.0	0	0	3.15	2.50	83.0	3.80	3.00	3.89	2.77	0.117	U	Nil	Nil
99	6	75.0	0	0	23.00	40.00	800.0	2.87	5.04	3.27	5.76		D	F	D

* P.H. = polyhalite. † P.S. = pentasalt. ‡ A. = anhydrite. § Gypsum instead of anhydrite.

boundary line between the pentasalt and anhydrite fields when magnesium sulfate is present in the system. Hill (8) has placed the pentasalt-anhydrite equilibrium at 5.78 g. of potassium sulfate per 100 grams of water. The data of experiments 69 and 80 in table 6 in which the equilibrium was approached from the pentasalt and anhydrite fields, respectively, gave an average of 5.64 g. of potassium sulfate per 100 grams of water. The concentration of the calcium sulfate, like the values found by Hill, was higher than 0.071, the figure Hill obtained by graphic interpolation.

Tests 71 to 78 and 81 to 82 are the result of an effort to discover the pentasalt-anhydrite boundary line at a concentration of 1.0 g. of magnesium sulfate per 100 grams of water. The extremely small concentration changes occurring in 32 to 33 days in these tests are additional proof of the slow rate of dissolution of pentasalt in a metastable region. Based solely on these data, the obvious conclusion would indicate this region as the stable pentasalt field; however, additional data prove this area to be the anhydrite field, as shown by figure 2. Experimental results prove that the pentasalt-anhydrite boundary line is very short and may therefore be determined with reasonable accuracy by a line connecting the pentasalt-anhydrite invariant point in the three-component system with the polyhalite-pentasalt-anhydrite invariant point in the four-component system.

Polyhalite-pentasalt-anhydrite invariant point

Several attempts were made to realize the polyhalite-pentasalt-anhydrite invariant point, but the slow rate of approach to equilibrium with both anhydrite and pentasalt as solid phases defeated such efforts. Innumerable compositions might easily be mistaken for the polyhalite-pentasalt-anhydrite equilibrium, since all three phases can exist for prolonged periods with little or no dissolution. This was apparently not fully appreciated by many previous investigators and resulted in errors in the location of equilibrium points and boundary lines. However, the intersection of the polyhalite-pentasalt and polyhalite-anhydrite curves defined by the present work, as indicated by the projections on the potassium sulfate-calcium sulfate and potassium sulfate-magnesium sulfate planes of figure 2, indicate values for the invariant point of 7.5 g. of potassium sulfate, 1.75 g. of magnesium sulfate, and 0.075 g. of calcium sulfate per 100 grams of water.

Polyhalite-anhydrite boundary line

The data collected to determine the polyhalite-anhydrite boundary line, given in table 7, are plotted in figures 2 and 5.

TABLE 7
Equilibrium in the system K_2SO_4 - $MgSO_4$ - $CaSO_4$ - H_2O at $100^\circ C$.
 Polyhalite-anhydrite boundary line

SAMPLE NO.	TIME IN THERMOSTAT	WEIGHT OF SOLIDS IN ORIGINAL MIXTURE			COMPOSITION OF LIQUID PHASE, IN GRAMS PER 100 GRAMS OF WATER					PETROGRAPHIC DATA ON SOLIDS		
					Initial		Final			F = Forming D = Dissolving		
		P.H.*	P.S.†	A.‡	K ₂ SO ₄	MgSO ₄	K ₂ SO ₄	MgSO ₄	CaSO ₄	P.H.	P.S.	A.
	days	grams	grams	grams	grams	grams	grams	grams	grams			
100	45	10.0		5.0	13.05	2.66	10.30	1.08	0.086	F		D
101	60	10.0		5.0	13.05	2.66	10.23	1.02	0.093	F		D
102	45	10.0		5.0	10.30	2.13	9.37	1.27	0.083	F		D
103	60	10.0		5.0	10.30	2.13	9.28	1.27	0.092	F		D
104	60	10.0	5.0	5.0	11.96	2.37	8.35	1.43	0.074	F	D	D
105	45	10.0		5.0	8.91	3.59	6.77	2.11	0.078	F		D
106	60	10.0		5.0	8.91	3.59	6.69	2.08	0.070	F		D
107	45	10.0		5.0	4.72	9.53	3.94	9.03	0.012	F		D
108	60	10.0		5.0	4.72	9.53	3.89	9.16	0.020	F		D
109	60	10.0		5.0	4.00	14.06	3.47	14.06	0.006	F		D

* P.H. = polyhalite. † P.S. = pentasalt. ‡ A. = anhydrite.

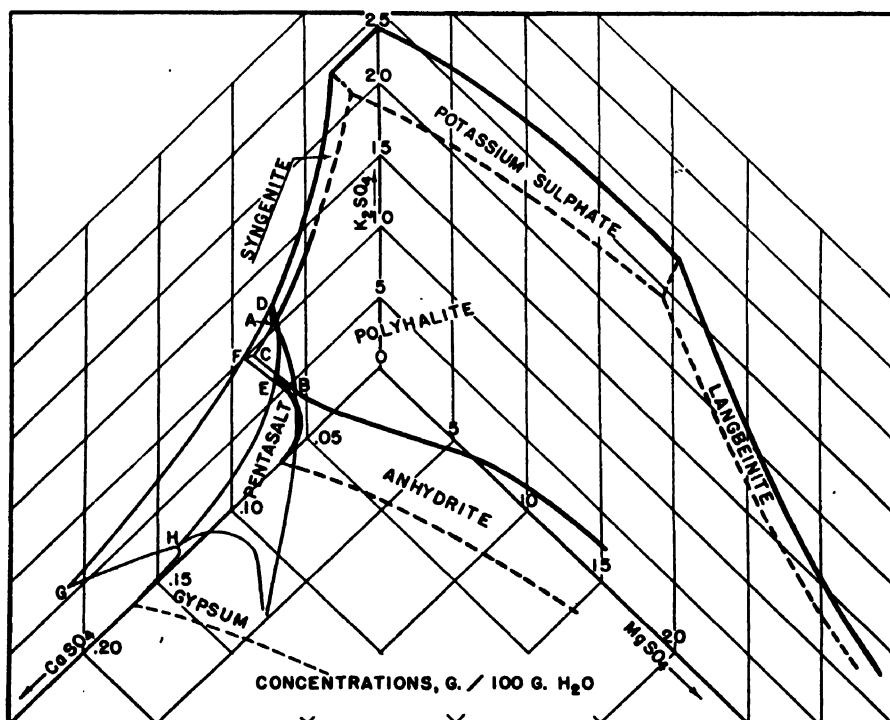


FIG. 6. Projection of space model representation of available data on the system potassium sulfate-magnesium sulfate-calcium sulfate-water at $100^\circ C$.

Space model of the system potassium sulfate-magnesium sulfate-calcium sulfate-water at 100°C.

In figures 2 to 5 the equilibrium data have been plotted on rectangular coordinates and liquid phase composition indicated in grams per 100 grams of water for pairs of components. In figure 6, the data have been utilized to represent a space model by isometric projection. Actual experimental points have, of course, been omitted. The 100°C. isotherm of Hill (8) has been used in constructing the potassium sulfate-calcium sulfate face of the figure and the corresponding isotherm of Starrs (12) for the potassium sulfate-magnesium sulfate face. An attempt has been made to

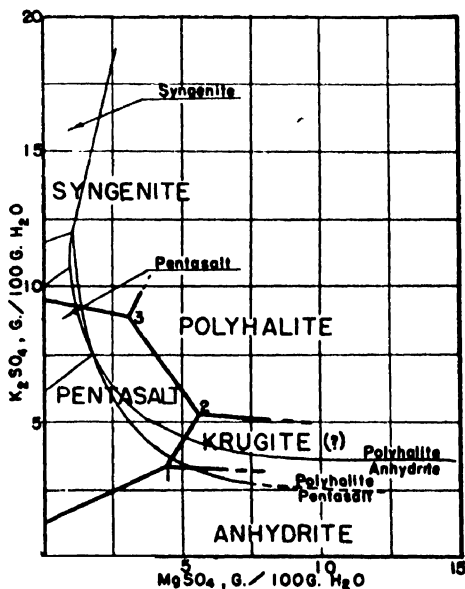


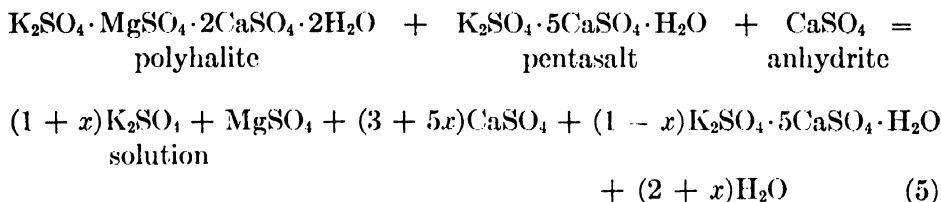
FIG. 7. Comparison of equilibria data of Geiger at 83°C. (heavy lines) and present work (light lines) at 100°C. by projection on the potassium sulfate-magnesium sulfate plane.

indicate the curvature of the surfaces where evidence for such curvature existed. It is evident that a much clearer conception of both the stable and the metastable equilibria may be had by reference to such a diagram.

Comparison of system at 100°C. with prior data for system at 83°C.

In figure 7 the stability field for pentasalt according to Geiger (6) at 83°C. has been superimposed on the potassium sulfate-magnesium sulfate plane on the equilibrium curves shown in figure 2 for 100°C. This field for pentasalt is considerably larger than that occurring at 100°C., a condition difficult to justify in that, according to Hill (8), the pentasalt field in the system potassium sulfate-calcium sulfate-water increases with in-

creasing temperature. Furthermore, it is evident that the boundary line 1-2 (figure 7) exactly represents the change in liquid-phase composition which would result from the dissolution of a solid phase such as polyhalite containing potassium sulfate and magnesium sulfate in equimolar proportions. If a mixture containing anhydrite, polyhalite, and pentasalt and a liquid phase corresponding to point 1 were permitted to react for a short period, the line or path 1-2 could be obtained from the following reaction:



where x represents an extremely small fraction of the pentasalt originally present. The stable phase being produced would be calcium sulfate in the form of anhydrite. This explanation agrees with observed facts, in that pentasalt may exist as a metastable phase under a wide range of conditions and that the polyhalite stability field expands with increase in temperature.

According to Geiger, krugite ($\text{K}_2\text{SO}_4 \cdot \text{MgSO}_4 \cdot 4\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), may exist at 83°C. as a stable phase. Other occurrences of this complex substance as a natural mineral have been reported by Schmidt (10) and van't Hoff (13). No such compound as krugite was encountered in any of the present tests made at 100°C. All attempts even under supposedly favorable conditions at 83°C. likewise failed to produce any krugite. Microscopic examination invariably disclosed the presence of polyhalite, but Ide (9) has shown recently from x-ray studies that "krugite" is a mixture of polyhalite and anhydrite. Chemical analysis, which has supplied the only suggestion of the existence of krugite, is applicable only in case the pure compound may be segregated. Obviously, a heterogeneous mixture of polyhalite, pentasalt, and anhydrite in the proper proportions might easily correspond to the composition of krugite.

Similarly it is found that the proposed boundary line 2-3 (figure 7), according to Geiger, separating the pentasalt and polyhalite fields has the exact slope corresponding to the decomposition of syngenite and formation of polyhalite. Similar paths are easily obtained at 100°C. by starting with mixtures of syngenite, polyhalite, and pentasalt in the region adjacent to the line 2-3. These facts would tend to condemn the practice of locating boundary lines by allowing an unstable mixture to react at a previously determined equilibrium point and fixing the resulting liquid phase com-

position change as an equilibrium boundary line. The path followed would invariably depend upon the relative rates of formation and decomposition of the stable and unstable phases respectively.

METASTABLE EQUILIBRIUM STUDIES AT 101-102°C.

A number of time-concentration experiments were made to obtain some information on the relative rate of approach to equilibrium in various regions. Owing to the exceptionally slow rate at which this system attains final stable equilibrium, most of these tests involved intermediate metastable phenomena tending toward stable equilibrium. From the results obtained in some of these experiments it has been possible to

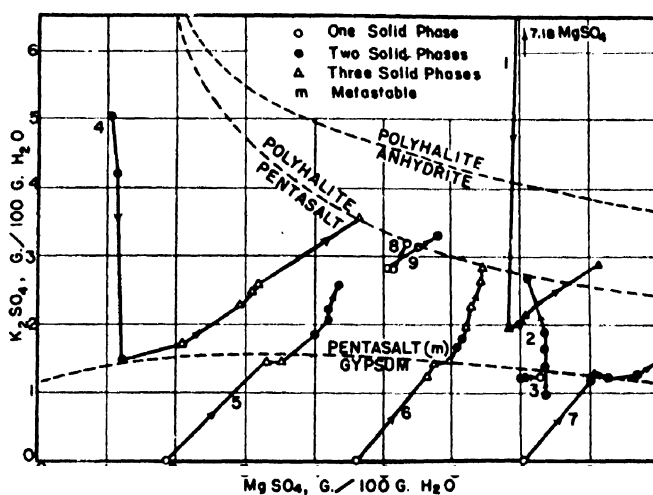


FIG. 8. Plotted data summarizing short-time tests made on the system potassium sulfate-magnesium sulfate-calcium sulfate-water at atmospheric boiling points of the respective solutions.

explain logically the behavior of certain of the long-time tests in which gypsum was added as the initial form of calcium sulfate. It has also been possible to interpret intelligently many of the phenomena encountered in the extraction of calcined polyhalite. The results of this class of experiments are given in table 8. These data have also been represented graphically in figure 8. As previously described, these tests represent the change in liquid and solid phases with lapse of time ranging in specific instances from intervals of a few hours up to several days. It should be noted that the temperatures at which all of these experiments were conducted were slightly above 100°C. All tests were made at the boiling point of the solution, which ranged from 101°C. to 102°C.

	4	5.0	1.22	7.04						
<i>Experiment 4:</i>										
750.0 g. H ₂ O	1	0	5.04	1.03						
37.5 g. K ₂ SO ₄	2	0.5*	4.20	1.15	10					Well-formed pentasalt
150.0 g. gypsum	3	1.5*	1.49	1.21	80					Pentasalt forming
75.0 g. polyhalite	4	2.5*	1.73	2.09	5-10					Pentasalt still forming
added after No. 3	5	7.0*	2.30	2.92						Solid phase nearly pure pentasalt
sample was taken	6	14.0*	2.48	3.08						Same as No. 5
	7	1.0	2.61	3.18						Same as No. 5
	8	2.0	3.55	4.61						Same as No. 5
<i>Experiment 5:</i>										
800.0 g. H ₂ O	1	0	0	1.87						
80.0 g. polyhalite	2	3.0*	1.43	3.28	65±	15±	20±	1		Hemihydrate in long well-formed needles; polyhalite corroded
20.0 g. pentasalt	3	12.0*	1.46	3.50	60±	40±	Nil	Nil		Pentasalt forming; hemihydrate disappearing
	4	1.0	1.62†		50±	50±	Nil	Nil		
	5	2.0	1.86	3.99	20±	80±	Nil	Nil		Pentasalt forming; polyhalite dissolving
	6	3.0	1.88†		5±	95±	Nil	Nil		
	7	5.0	2.08	4.19	1±	99±	Nil	Nil		Few fragments of polyhalite left
	8	7.0	2.18	4.22						
	9	9.0	2.23	4.18						
	10	12.0	2.35	4.26						
	11	15.0	2.57	4.33						

• Time in hours.

† Expressed in percentage instead of grams per 100 grams of water.

It also contains the CaSO_4 present in solution.

<i>Experiment 8:</i> 800.0 g. H_2O 75.0 g. pentasalt	6	4.0	1.92	10.06						Polyhalite corroded; hemihydrate corroding; anhydrite forming Same as No. 6 Same as No. 6
	7	6.0	2.44	11.90						
	8	8.0	3.11	14.68						
	1	0	2.84	5.13						Solid phase is all pentasalt
	2	0.5	2.89	5.12						Same as No. 2
	3	1.0	3.01	5.22						Same as No. 2
	4	2.0	2.98	5.24						Same as No. 2
	5	3.0	3.02	5.24						Same as No. 2
<i>Experiment 9:</i> 800.0 g. H_2O 75.0 g. polyhalite	6	5.0	3.09	5.25						Little if any change apparent under the microscope
	7	7.0	3.18	5.33						
	1	0	2.87	5.04						Polyhalite unchanged
	2	1.0	3.17	5.52						Same as No. 2
	3	2.0	3.07	5.56						Same as No. 2
	4	3.0	3.19	5.55						A few crystals of pentasalt have appeared
	5	5.0	3.27	5.72						Slight increase in amount of pentasalt
	6	6.0	3.27	5.76						
<i>Experiment 10:</i> 800.0 g. H_2O 75.0 g. polyhalite	1	0	5.95	0					40	Syngenite showing evidence of solution
	2	1.0*	6.09	0.30	60				15	Pentasalt forming; syngenite decomposing
	3	4.0*	6.06	0.39	70	15				Occasional crystal of pentasalt
	4	0.5	6.44	0.58	55	45				Pentasalt increasing
	5	1.0	6.52	0.70	50	50				
	6	2.0	8.62	1.12						Same as No. 6
	7	4.0	10.16	1.80						Same as No. 6
	8	6.0	10.22	1.91						

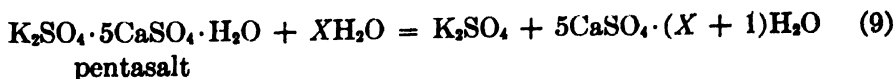
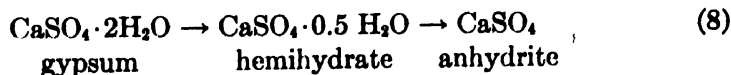
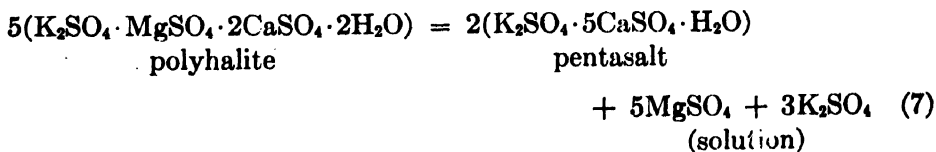
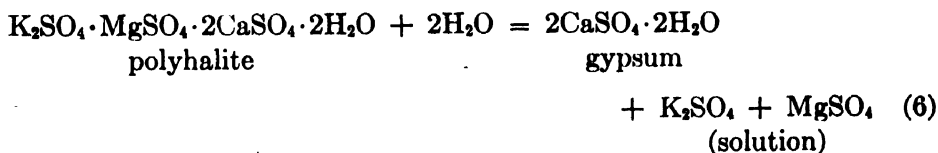
Gypsum-pentasalt metastable equilibrium

Experiment 1 was made to explain the relatively large change in liquid-phase composition encountered in an experiment in which solid gypsum, together with pentasalt and a few polyhalite "seeds," had been added to a solution of potassium and magnesium sulfates containing 6.0 g. of each per 100 g. of water. The results obtained in this test showed that the gypsum added to the original mixture reacted rapidly with the potassium sulfate to precipitate pentasalt. This reaction proceeded so rapidly that the liquid phase was altered to a composition probably outside the boundaries of the polyhalite field. The subsequent disappearance of practically all of the polyhalite present, together with the increase in the magnesium sulfate in the liquid phase, confirms this belief. Subsequent experiments indicated the metastable gypsum-pentasalt equilibrium to be at a lower concentration than was reached in this test, and therefore likely to represent the state which the system was tending to approach. This assumption was checked further by experiments 2 and 3. In the former test 80.0 g. of gypsum was added to the solution containing 2.67 g. of potassium sulfate and 7.08 g. of magnesium sulfate per 100 g. of water. A decrease in potassium sulfate occurred, owing to the formation of pentasalt as disclosed by the petrographic microscope. Obviously this test comprises an approach from supersaturation with respect to potassium sulfate. Experiment 3 shows the results of an attempt at approach from undersaturation with respect to potassium and calcium sulfates. As may be seen by reference to the data given in table 8, the solution composition showed no apparent change in composition in 12 days; but the gypsum was partly converted to hemihydrate. Microscopic examination usually showed a rapid transformation of the gypsum to hemihydrate and evidence of a subsequent slow change to anhydrite in many experiments made in this region. This fact is evidence to show that this liquid-phase composition is in the metastable gypsum, or hemihydrate fields. These two experiments fix the limits of the gypsum-pentasalt boundary as being between 1.22 and 1.38 g. of potassium sulfate per 100 g. of water in this portion of the diagram.

Experiment 4 is an experiment similar to No. 1 of this series, except that the initial starting composition is in a different region and a larger quantity of polyhalite was added to the reaction mixture after $1\frac{1}{2}$ hours. From the behavior of the liquid phase and from the nature and appearance of the solid phases the changes taking place can be followed. During the first $1\frac{1}{2}$ hours pentasalt was formed rapidly, thereby removing potassium sulfate from solution. As soon as the polyhalite was added it began to decompose, but pentasalt continued to form for the next 5 or 6 hours. This test would tend to prove that polyhalite was unstable in this region

and pentasalt was the stable phase. However, between samples 5 and 7 the liquid-phase composition corresponds to the simple decomposition of polyhalite without any apparent formation of pentasalt. This is of special significance, since it gives a clue to whether pentasalt is the final stable phase in this region. Stoichiometric calculations indicate that all of the polyhalite added to the initial mixture would have to decompose to effect the liquid-phase concentration represented by sample 6. The petrographic microscope fails to disclose the presence of any polyhalite at this point. Unfortunately, subsequent solution changes are only explainable as due to evaporation losses. It may be concluded, therefore, that as we are able to produce pentasalt up to a point falling somewhere between sample 4 and sample 5, this region is possibly the stable field for pentasalt or at least a metastable region for the salt. Other data on this region would lend credence to the latter assumption.

Experiments 5, 6, and 7 show the results obtained when mixtures of polyhalite and pentasalt or polyhalite alone (experiment 7) are decomposed with solutions containing the indicated amounts of magnesium sulfate but no potassium sulfate. These tests were made to see if it would be possible to realize the gypsum-pentasalt or the gypsum-pentasalt-polyhalite metastable equilibria. No conclusive evidence of attaining the latter point was obtained, but every test showed an indication of passing through the former metastable boundary. The various reactions that occur can be explained from consideration of the concentration changes of the liquid phase and from the nature of the solid phase. The following reactions express the changes:



$$X = (-1 \text{ to } 9)$$

Apparently in all three experiments the reaction expressed by equation 6 takes place until the potassium sulfate in solution is increased to approximately 1.35 g. per 100 grams of water. This concentration is reached in from 3 to 4 hours. Each curve then shows a slight break, which has been interpreted as indicating that the reactions as given by equations 7 and 8 enter the picture. Microscopic evidence shows that the gypsum rapidly disappears by replacement with hemihydrate, which in turn is much more slowly replaced by anhydrite. These breaks are at, or probably very near, the gypsum-pentasalt equilibrium. Pentasalt apparently forms for several days at the expense of the polyhalite until the latter disappears. This reaction is more pronounced in test 5 than in test 6 or 7. As the polyhalite is exhausted the pentasalt formed by equation 7 decomposes in turn, according to equation 9. The actual attainment of a form of calcium sulfate which completely satisfies the physical constants for natural anhydrite has proved difficult to realize in these short-time experiments, since anhydrite forms at an extremely slow rate. However, all of the evidence points toward this region as representing the stability field for anhydrite.

Experiments 8 and 9 were made in an effort to define the limits of the pentasalt (or anhydrite) field and of the polyhalite field. A quantity of synthetic pentasalt was extracted in experiment 8 for a total of 7 days with a potassium sulfate-magnesium sulfate solution, while polyhalite was similarly extracted for a 6-day period. Data from previous experiments indicate that 6 or 7 days is too short a time to permit intelligent conclusions in regard to the final stable phases. Both of the initial solid phases gave evidence of decomposition, although of a small order. The behavior of the pentasalt in experiment 8 agrees with the behavior of pentasalt over a large area in this region in many of the 30-day tests, in that a very slight decomposition occurs, accompanied by a slight increase in potassium sulfate in solution. The small amount of calcium sulfate that should appear in the solid phase would be easily overlooked, particularly if present as hemihydrate in process of conversion to anhydrite. The results of experiment 9 show that polyhalite is the unstable phase, and the appearance of a few crystals of pentasalt would indicate this region as probably metastable with respect to pentasalt. However, hemihydrate in process of change to anhydrite has been identified at lower potassium sulfate concentrations and may also be present here. This inherent difficulty was probably the reason why Geiger concluded that he had produced "krugite" as a new solid phase at about this composition but at 83°C.

The next experiment (No. 10) is an excellent example which illustrates the danger of fixing the last solid phase obtained in periods ranging from 1 to 8 days as the final stable phase. In the test polyhalite decomposed, forming first syngenite and finally pentasalt. Data presented elsewhere have proved that pentasalt is not the final stable phase in the region of

sample 3 but that anhydrite is, and that both syngenite and pentasalt are able to exist for more or less prolonged periods as metastable phases.

SUMMARY AND CONCLUSIONS

As the result of a considerable number of tests in the system potassium sulfate-magnesium sulfate-calcium sulfate-water the tentative stability fields for syngenite, pentasalt, polyhalite, and anhydrite have been defined within the limits of 17.0 g. of potassium sulfate and 14.0 g. of magnesium sulfate per 100 grams of water at 100°C.

The actual attainment of the final equilibria was found to be extremely slow, and in some instances was incomplete after 60 and 69 days. Metastable equilibria were encountered in nearly every portion of the area ex-

TABLE 9

*Summarized data on important equilibrium points in the system
 K_2SO_4 - $MgSO_4$ - $CaSO_4$ - H_2O at 100°C.*

POINT	SOLID PHASES	LIQUID PHASE COMPOSITION IN GRAMS PER 100 GRAMS OF WATER		
		K_2SO_4	$MgSO_4$	$CaSO_4$
		grams	grams	grams
A	Polyhalite-syngenite-pentasalt	12.1	0.9	0.08
B	Polyhalite-pentasalt-anhydrite	7.5	1.7	0.075
C (m)	Polyhalite-syngenite-anhydrite	10.7	0.8	0.093
D	Syngenite-pentasalt	11.7	0	0.075
E	Pentasalt-anhydrite	6.0	0	0.07
F (m)	Syngenite-anhydrite	10.0	0	0.092
G (m)	Syngenite-gypsum	5.7	0	0.21
H (m)	Pentasalt-gypsum	1.1	0	0.137

Note: Points to which the suffix "(m)" is added are metastable.

plored, and in certain cases were distinguished from stable equilibria only by the utmost precautions. Invariably, the short-time tests of a few hours or even several days resulted in metastable conditions. Pentasalt ($K_2SO_4 \cdot 5CaSO_4 \cdot H_2O$) was found to persist in a large portion of the area studied and particularly when initially placed in the anhydrite field. Natural anhydrite reacted at a very slow rate also, but the limited solubility and the fact that all of the calcium sulfate must pass through the solution phase to be available for subsequent reaction explains this phenomenon.

The form in which the calcium sulfate is added to the mixtures used in the study of this system is extremely important. The stable form is, of course, anhydrite. If gypsum is used, metastable equilibria are obtained and the gypsum slowly alters to hemihydrate and finally anhydrite. Mixtures having optical properties intermediate between hemihydrate and anhydrite were frequently noted.

From the data collected during this investigation many of the results obtained during the extraction of calcined polyhalite at 100°C. are easily explained, and a much clearer conception of reactions taking place within the specified region is possible.

To facilitate the determination of the various equilibria involving some form of calcium sulfate either as such, or as a component of the solid phase in the three- and four-component systems, table 9 has been prepared. The location of the various points tabulated may be clearly understood by referring to figure 6.

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DECOMPOSITION AND SYNTHESIS OF HYDROGEN IODIDE BY ALPHA PARTICLES¹

KEREN GILMORE BRATTAIN²

School of Chemistry, University of Minnesota, Minneapolis, Minnesota

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The radiochemical decomposition and synthesis of hydrogen iodide have been studied by Vandamme (15) at 20°C. and 100°C., respectively. He used comparatively small amounts of radon. The author also studied these reactions under somewhat different conditions. The decomposition of hydrogen iodide by alpha particles was determined by two methods: (1) the rate of reaction was followed by pressure measurements, which were made at 25°C.; (2) closed-system experiments were performed at 27°, 100°, and 200°C., and the amount of reaction determined by chemical analysis at the end of the experiment. Similar closed-system experiments on synthesis were made at temperatures ranging from 25°C. to 200°C.

EXPERIMENTAL PROCEDURE

In the first set of decomposition experiments the radon and hydrogen iodide were enclosed in a small bulb connected to a mercury manometer. The apparatus and procedure were the same as those employed by Lind and Bardwell (11). There was practically no contamination of the mercury until the experiment was well along. A phosphoric acid lubricant (13) was used on the stopcocks in all systems in which hydrogen iodide was present. The closed-system decomposition experiments were performed in reaction bulbs, with two capillary tubes connected along one diameter. These bulbs, which had an approximate volume of 60 cc., have been described by Truesdale and Lind (14). The experimental procedure was as follows: Small fragile glass ampoules filled with radon were sealed into the reaction bulb. The bulb was then connected to a high-vacuum system and pumped for several hours. During this time it was washed with small volumes of hydrogen iodide. An approximate amount of hydrogen iodide was then frozen in the reaction bulb and the bulb was sealed off. Extreme care was taken to obtain a capillary tip that could be broken readily later. The ampoule containing the radon was broken,

¹ This article is based upon a thesis submitted by Keren Gilmore to the Graduate School of the University of Minnesota in partial fulfillment of the requirements for the degree of Doctor of Philosophy, August, 1932.

² Present address: 270 West 11th Street, New York City.

and the reaction bulb placed in a constant-temperature apparatus at once. A small electrically heated oven, constant to within $\pm 1^\circ\text{C}$., was used for all experiments with the exception of those run at 25°C . and 27°C . In these cases the bulbs were placed in a constant-temperature water bath. At the end of the experiment the bulbs were quickly cooled to room temperature, and one of the tips was broken off under a solution of potassium iodide. A sufficient amount of the solution entered the bulb to dissolve the iodine. The second tip was broken, and the bulb rinsed with small amounts of potassium iodide. The resulting solution was used for the determination of both the iodine and the remaining hydrogen iodide. First the amount of iodine present was determined by titration with sodium thiosulfate to a water-white solution. The acid was then titrated with sodium hydroxide, bromothymol blue being used as the indicator. A blank run containing no radon accompanied each experiment. From this the amount of thermal reaction was obtained.

The procedure used for the synthesis experiments was very similar to that of the closed-system decomposition experiments described above. A fragile glass ampoule containing iodine and one containing radon were introduced into the reaction bulb before it was sealed onto the vacuum line. The bulb was pumped and washed with hydrogen. A known volume of hydrogen was introduced in the reaction bulb from a Ramsay buret, and the bulb sealed off. The experiment was then performed in the manner given above.

The following method was used for preparing the hydrogen iodide used in the decomposition experiments: First, a fuming solution of hydriodic acid was prepared, in an all-glass system, by dropping water on phosphorus and iodine. The resulting gas was passed through four traps cooled with an ice-salt mixture, and then into an absorption bulb containing distilled water. This bulb was also cooled by an ice-salt mixture. The solution thus prepared was stored in a refrigerator. The hydrogen iodide was prepared from the stock solution as it was needed by the following series of vacuum distillations. Twenty cubic centimeters of the hydriodic acid was placed in a distilling flask, and the flask was sealed onto a high-vacuum line. The pumps were well protected with liquid air. The solution was frozen with carbon dioxide snow. The air was thoroughly pumped out of the system, and then the solution was allowed to warm up slowly. The resulting gas was passed through a trap cooled with solid carbon tetrachloride, which removed most of the water vapor, then dried over phosphorus pentoxide. The hydrogen iodide was frozen down with liquid air and the system well pumped. The gas was then distilled through two traps cooled with carbon dioxide snow, and finally frozen in the reaction bulb with liquid air. For the decomposition experiments the hydrogen was prepared by the electrolytic decomposition of a potassium hydroxide solution. The gas from the generator was passed over palladinized asbes-

tos, heated to 300°C., dried over phosphorus pentoxide, and stored in a 2-liter bulb. This bulb had been pumped and flushed with hydrogen several times previous to the storage. The iodine was purified by three consecutive sublimations (9) of chemically pure iodine obtained from the Mallinckrodt Company. The resublimed iodine was dried over calcium chloride in an ungreased desiccator and stored in a dark glass-stoppered bottle. For experimental use small quantities of the iodine were placed in fragile glass ampoules, pumped for an hour, and then sealed off.

TABLE 1
Pressure decomposition experiments

TOTAL P				$N_{HI} \times 10^{10}$	$N_{H_2} \times 10^{10}$	$\frac{M_{HI}}{\text{DECOMPOSED}} \times 10^{10}$	$\frac{M_{HI}}{N_{HI}}$
Expt. No. I. Volume = 3.99 cm. ³ ; $T = 25^\circ\text{C}.$; $R = 0.984$ cm.; $E_0 = 125.9$ mc.							
hours							
0	597	597					
1.0	558	520	38	0.161	0.000	1.00	6.21
2.0	514	431	83	0.295	0.000	2.16	7.32
3.0	482	367	115	0.405	0.003	.00	7.42
4.0	453	309	144	0.496	0.007	.74	7.54
8.0	405	213	192	0.764	0.030	.99	6.54
12.	390	182	208	0.965	0.052	.39	5.58
18.	370	143	227	1.20	0.088	.90	4.90
24.	356	115	241	1.38	0.123	.27	4.54
36.	327	57	270	1.57	0.208	.02	4.47
Expt. No. II. Volume = 11.50 cm. ³ ; $T = 25^\circ\text{C}.$; $R = 1.40$ cm.; $E_0 = 103.8$ mc							
0	676	676					
1.0	657	638	19	0.228	0.006	1.44	6.31
5.3	587	498	89	1.03	0.020	6.67	6.48
9.0	540	403	136	1.69	0.041	10.3	6.08
18.	467	258	209	2.54	0.106	15.7	6.20
25.	425	174	251	2.94	0.160	18.9	6.43
45.	370	64	306	3.41	0.371	23.0	6.73
69.	359	42	317	3.64	0.533	23.2	6.37

The sodium thiosulfate used in the titrations was resublimed, and the solution standardized against a weighed amount of resublimed iodine. A water-white solution was used as the end point. The normality of the solution was redetermined at various intervals. The sodium hydroxide solution was standardized against Mallinckrodt's reagent quality oxalic acid with phenolphthalein as the indicator.

EXPERIMENTAL RESULTS

The experimental results are given in tables 1, 2, and 3. The last four columns in table 1 will be discussed later. In tables 2 and 3 the pressure

of hydrogen iodide was calculated from the chemical analysis. The pressure of hydrogen in table 2 was calculated from the iodine analysis, since equal amounts of hydrogen and iodine are formed by the decomposition of hydrogen iodide. In table 3 the hydrogen pressure was calculated from the Ramsay buret measurements. The vapor pressure of solid iodine was computed by the method of Giauque (4), and that of liquid iodine was

TABLE 2
Closed-system decomposition experiments

EXPT. NO.	REACTION TEMPERATURE	TIME	BULB VOLUME	INITIAL RADON	P_{HI}^0	P_{H_2} FINAL	P_{I_2} FINAL
	°C.	hours	cm. ³	millicuries	mm.	mm.	mm.
1.....	27.5	53.0	54.9	41.2	383.	49.7	0.3
2.....	27.5	53.2	57.2	31.7	806.	87.8	0.3
3.....	100.	88.9	57.2	30.1	252.	28.4	28.4
4.....	203.	63.8	54.9	13.9	215.	12.5	12.5
5.....	203.	63.5	57.2	15.1	212.	11.2	11.2

TABLE 3
Synthesis experiments

EXPT. NO.	REACTION TEMPERATURE	TIME	BULB VOLUME	INITIAL RADON	$P_{\text{H}_2}^0$	$P_{\text{I}_2}^0$	P_{HI} FINAL
	°C.	hours	cm. ³	millicuries	mm.	mm.	mm.
1.....	200	58.9	58.3	64.4	323.	285.	26.8
2.....	200	59.0	57.0	60.3	320.	287.	27.3
3.....	174	211.	58.4	118.9	368.	358.	80.6
4.....	225	213.	58.5	103.3	346.	317.	81.6
5.....	120	209.	56.9	31.6	506.	109.	27.9
6.....	150	186.	58.4	112.0	530.	294.	99.4
7.....	200	183.	57.1	126.1	581.	353.	129.
8.....	121	196.	56.9	93.9	570.	115.	74.0
9.....	100	213.	56.4	103.5	397.	45.9	51.5
10.....	174	165.	56.9	108.6	676.	70.3	63.0
11.....	100	208.	56.4	94.2	543.	45.9	59.6
12.....	81.0	208.	57.0	100.0	687.	15.9	52.7
13.....	54.7	192.	57.0	100.2	537.	3.0	22.0
14.....	25.0	216.	58.5	117.2	520.	0.3	4.5
15.....	25.0	238.	58.4	110.9	535.	0.3	9.4

obtained from the data of Ramsay and Young (12). In all the synthesis experiments performed at temperatures below 150°C. a sufficient amount of iodine was present to maintain a constant pressure. In the experiment performed at 150°C. the pressure of iodine was constant only during the first part of the run. The vapor pressure of iodine at this temperature is 294 mm. The amount of iodine introduced was sufficient to give a pres-

sure of 309 mm. The final pressure of iodine was 259 mm. The initial pressure of iodine for all the synthesis experiments above 150°C. was obtained by adding one-half the calculated pressure of hydrogen iodide to the final pressure of iodine obtained from analysis. The number of molecules of hydrogen iodide where given as yields has been corrected for thermal reaction. These corrections were small.

CALCULATIONS AND RESULTS

In order to analyze the data it is necessary to determine some measure of the excitation produced by the alpha particles in each of the gases present. The accepted method for doing this is to calculate the number of ion pairs formed. The total number of ion pairs formed in the gaseous mixture was obtained from the following equation.

$$N_i = N_0 E g F' k(r)^{\frac{1}{2}}$$

where N_i = total number of ion pairs formed,

N_0 = number of alpha particles per curie of radon (1.764×10^{10}) (6),

E = number of curies of radon decomposed (corrected for non-equilibrium decomposition) (14),

g = specific ionization in gaseous mixture (7),

F' = efficiency factor (6), and

$k(r)^{\frac{1}{2}}$ = number of ion pairs produced by an alpha particle in its range in air (N.T.P.) (1.55×10^6) (6).

A slight modification of this equation was used for the calculation of the pressure experiments. An average F' was calculated for each interval. This value was then used in calculating the number of ion pairs formed during each interval. The total number of ion pairs at any time was then obtained by addition.

The number of ion pairs formed in each component of the system was calculated from the following equation,

$$N_a = N_i \frac{s_a g_a p_a}{\sum s g p} \quad (2)$$

where s = stopping power and p = partial pressure of the component. The summation is over all components present.

In the closed-system experiments the arithmetical mean of the initial and final pressures was used in all calculations. The stopping power of iodine was taken as 3.70 (5) and that of hydrogen iodide as 1.97, computed as an additive property from values of stopping powers of hydrogen and iodine. The values 1.31 (8) and 1.29 (10) were used for the specific ionization of iodine and hydrogen, respectively.

The results of the calculations for the decomposition of hydrogen iodide

are given in tables 1 and 4. In figure 1 the number of molecules of hydrogen iodide decomposed is plotted against the number of hydrogen

TABLE 4
Decomposition results

EXPT. NO.	RADON DECOMPOSED <i>millicuries</i>	$N_{HI} \times 10^{19}$	$N_{H_2} \times 10^{-19}$	$N_{I_2} \times 10^{19}$	$M_{HI} \times 10^{-19}$	$\frac{M_{HI}}{N_{HI}}$
1.....	13.5	3.28	0.02	0.005	17.7	5.38
2.....	10.4	5.38	0.03	0.004	32.5	6.04
3.....	14.6	1.84	0.01	0.22	8.37	4.55
4.....	5.28	0.450	0.001	0.027	2.52	5.60
5.....	5.71	0.490	0.001	0.026	2.32	4.74
1*.....	13.1	5.06	0.02	0.009	36.9	7.28
2*.....	12.4	6.26	0.03	0.008	46.0	7.33
3*.....	10.4	6.10	0.03	0.006	59.1	9.69
1*.....	7.98	4.62	0.01	0.004	30.8	6.67
2*.....	7.95	3.26	0.01	0.005	26.6	8.16
3*.....	8.22	3.62	0.01	0.005	20.9	5.78
4*.....	8.25	1.20	0.004	0.004	10.8	9.03

* Calculated from Vandamme's data.

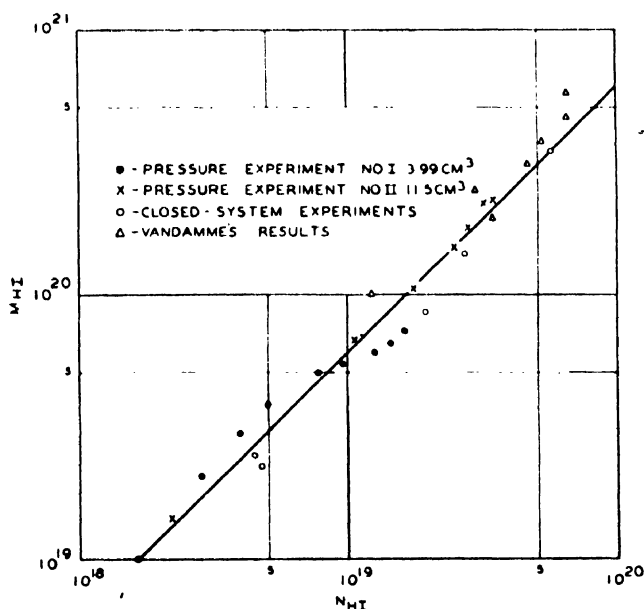


FIG. 1. Decomposition of hydrogen iodide

iodide ion pairs. It is seen that on the whole the amount of decomposition is proportional to the hydrogen iodide ion pairs, and that for each

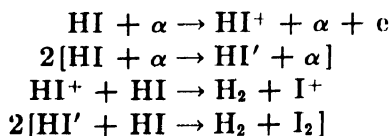
ion pair 6+ molecules of hydrogen iodide are decomposed. The various points scatter to some extent, and Vandamme's results are on the average a little higher than the author's. This last fact could be caused by differences in radon standards. The simplest explanation of the reaction is that, on an average, for each hydrogen iodide ion pair produced by an alpha particle two activated hydrogen iodide molecules are also produced.

TABLE 5
Synthesis results

EXPT. NO.	$N_{H_2} \times 10^{10}$	$N_{HI} \times 10^{10}$	$N_{I_2} \times 10^{10}$	$M_{I_1} \times 10^{-10}$	$M_{HI} \times 10^{10}$	$\frac{M_{HI}}{M_{I_1}}$ OBSD.	$\frac{M_{HI}}{M_{I_1}}$ CALCD.
1.....	0.333	0.149	5.92	33.2	2.71	0.082	0.094
2.....	0.312	0.145	5.64	32.7	2.69	0.083	0.090
3.....	1.64	2.02	32.4	42.7	10.1	0.235	0.261
4.....	1.19	1.59	22.0	33.6	8.11	0.241	0.217
5.....	0.626	0.187	2.78	15.4	3.79	0.246	0.260
6.....	2.26	2.35	25.3	37.5	12.9	0.343	0.322
7.....	2.44	3.04	28.8	37.8	13.9	0.367	0.298
8.....	2.04	1.45	8.60	16.1	10.3	0.640	0.597
9.....	1.64	1.16	3.98	6.75	6.95	1.03	1.03
10.....	2.24	1.13	3.72	6.74	7.80	1.16	1.61
11.....	2.02	1.20	3.51	6.75	8.32	1.23	1.35
12.....	2.88	1.20	1.38	2.49	8.23	3.30	5.65
13.....	2.37	0.518	0.266	0.503	3.71	7.39	25.9
14.....	3.16	0.147	0.038	0.059	0.83	14.1	332.
15.....	3.18	0.298	0.036	0.059	0.89	15.0	325.
1*.....	0.206	0.031	1.29	20.8	1.88	0.090	0.074
2*.....	0.218	0.029	1.18	20.6	1.94	0.094	0.078
3*.....	0.414	0.056	1.24	19.0	3.27	0.172	0.145
1*.....	0.036	0.005	0.614	23.4	0.787	0.034	0.017
2*.....	0.171	0.012	0.625	20.1	1.51	0.075	0.060
3*.....	0.245	0.013	0.556	18.4	1.64	0.089	0.090

* Calculated from Vandamme's data.

Each of these three reacts with a neutral hydrogen iodide molecule, thus giving a net result of six molecules decomposed.



The reaction, of course, may be much more complicated, but this mechanism is sufficient to explain the facts.

In these decomposition experiments the number of hydrogen ion pairs was always so small as to be negligible, except possibly in the last two or

three points of the pressure runs. Consequently no conclusions can be drawn from these data as to the effect of the hydrogen ion pairs on the reaction. The highest pressure of iodine occurred in the closed-system experiment No. 3. In this experiment the average iodine pressure was one-fifteenth that of the average hydrogen iodide pressure. An iodine pressure of this relative magnitude appears to have no effect on the yield, provided one considers only the ion pairs formed in hydrogen iodide.

The calculated results for the synthesis of hydrogen iodide are given in table 5. These data are not so easy to analyze. The reasons for this are obvious. One has a complicated mixture of three components and the ion pairs due to each component. In a general way one can say that the amount of synthesis should be some function of the various types of ion pairs present.

$$M_{\text{HI}} = F(N_{\text{H}_2}, N_{\text{HI}}, N_{\text{I}_2}) \quad (3)$$

where M_{HI} is the yield. In analyzing these data the author found it a distinct advantage to consider ratios instead of absolute magnitudes. The particular ratios that were found useful were the various magnitudes divided by the average number of molecules of iodine present (M_{I_2}). The synthesis results consist of the measurements of the yield at the end of a long run. Since the number of ion pairs of the components varies throughout the run, and since back reaction is always possible, the yield is probably given accurately only in terms of a complicated integral. However, an attempt was made to analyze the data using average values. From the results of this analysis the author has come to the conclusion that this procedure is justified where these data are concerned.

As a first trial the author made the assumption that only the hydrogen ion pairs were effective in the synthesis of hydrogen iodide, and that the ion pairs of iodine and hydrogen iodide could be neglected. Figure 2 is a plot of $M_{\text{HI}}/M_{\text{I}_2}$ versus $N_{\text{H}_2}/M_{\text{I}_2}$. The data of Vandamme and of the author give results which follow a straight line. This relationship can be approximately represented by the following equation.

$$\frac{M_{\text{HI}}}{M_{\text{I}_2}} = k \left(\frac{N_{\text{H}_2}}{M_{\text{I}_2}} \right)^{\frac{1}{2}} \quad (4)$$

where k is a constant. Since the yield is not proportional to the hydrogen ion pairs, it would appear that there were other factors involved in the reaction. Therefore the assumptions were too simple. The relationship does indicate, however, that there is no large discrepancy between the results of Vandamme and those of the author. An attempt was made to see if a reasonable amount of back reaction would account for the fact that the yield is not proportional to the hydrogen ion pairs. Farkas and Bonhoeffer (3) report that in equal mixtures of hydrogen iodide and iodine a

hydrogen atom combines one hundred times more readily with an iodine molecule than with a hydrogen iodide molecule. It was found that a back reaction based on the probability of a hydrogen atom reacting fifty to one hundred times more readily with iodine than with hydrogen iodide would affect only the last few points for large values of M_{HI}/M_{I_2} . These points are seen to deviate from the straight line anyway, and in a direction which could be accounted for by a back reaction. No assumed value of the relative probability of these two reactions would make the yield proportional to the hydrogen ion pairs over any appreciable range.

The next logical assumption which might be made is that the hydrogen iodide ion pairs as well as those of the hydrogen affect the yield. An examination of the possible reactions of an excited hydrogen iodide mole-

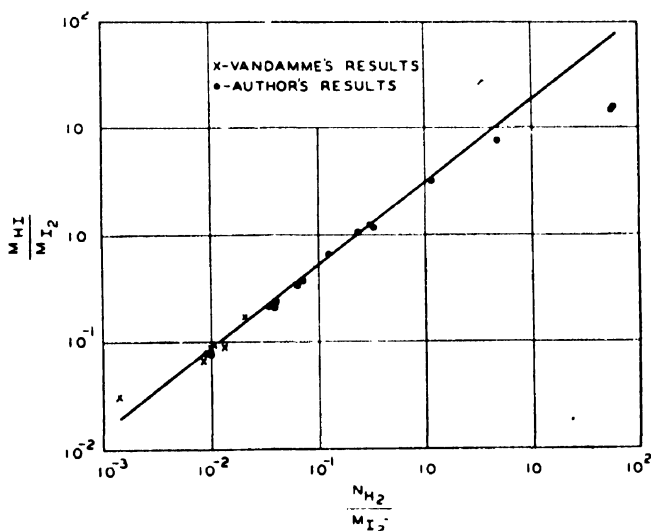


FIG. 2. Synthesis of hydrogen iodide. M_{HI}/M_{I_2} plotted against N_{H_2}/M_{I_2}

cule indicates that the products of ionization or activation of hydrogen iodide could at most react with hydrogen or iodine in such a way that the net hydrogen iodide formed or decomposed is zero. Therefore the only effect of the hydrogen iodide ion pairs would be the decomposition of neutral molecules of hydrogen iodide. The simplest way of considering the effect of both the hydrogen and hydrogen iodide ion pairs is to assume that it is proportional to the number of ion pairs of each gas present.

$$\frac{M_{HI}}{M_{I_2}} = a \frac{N_{H_2}}{M_{I_2}} + b \frac{N_{HI}}{M_{I_2}} \quad (5)$$

where a and b are constants. The values of the constants which gave the best correlation were $a = 10$ and $b = -4$. However, the correlation at

best was very poor. Work by Eyring, Hirschfelder, and Taylor (1, 2) would indicate that six molecules of hydrogen iodide should be formed per hydrogen ion pair instead of ten. An examination of the data on the basis of the above correlation made it appear that the reaction was also dependent upon the number of ion pairs formed in iodine.

An assumption was then made that each of the different ion pairs present affected the synthesis according to the following relationship.

$$\frac{M_{HI}}{M_{I_2}} = a \frac{N_{H_2}}{M_{I_2}} + b \frac{N_{HI}}{M_{I_2}} + c \frac{N_{I_2}}{M_{I_2}} \quad (6)$$

It was found that the data of Vandamme and of the author could be well represented by equation 6, when the constants a , b , and c have the values

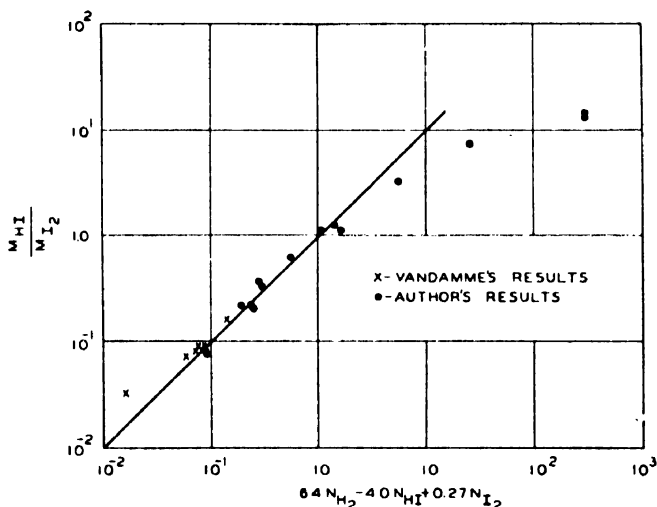


FIG. 3. Synthesis of hydrogen iodide

6.4, -4.0 , and 0.27 , respectively (table 5, column 8). A plot of this relationship using these constants is given in figure 3. The relationship indicates that 6.4 molecules of hydrogen iodide are formed per hydrogen ion pair. The value of the constant b is surprisingly high. However, it is possible that for every hydrogen iodide ion pair an average of two ionized or activated hydrogen iodide molecules will react with neutral hydrogen iodide molecules, thus causing a counter reaction. If the assumptions underlying equation 6 are correct, the data indicate that a small fraction of the iodine ion pairs react with hydrogen to form hydrogen iodide. There are two possible reactions which might explain this effect. First, a neutral hydrogen molecule may cluster with an I_2^+ ion. The reaction of an electron with this cluster could give two molecules of hydrogen

iodide and excess energy. Second, it is also possible for an excited iodine molecule to react with a hydrogen molecule to form hydrogen iodide and excess energy. The explanation of the data by equation 6 requires only that one excited or ionized iodine molecule react for every seven ion pairs formed in iodine.

We see in figure 3 that the last few points, for large values of M_{HI}/M_{I_2} , still deviate from the straight line. This is probably the effect of the back reaction, which has been discussed in the first attempt to analyze these data. The deviation of these points could also be caused by the fact that in these experiments the pressure of the iodine is so low that a large portion of the excited hydrogen may become deactivated without coming in contact with iodine molecules. The number of the points and the accuracy of the data in this region are probably not sufficient to decide definitely between these two possibilities. The data, however, are not inconsistent with the probability that the activated hydrogen reacts one hundred times more readily with iodine than with hydrogen iodide.

The author has also attempted to analyze these data on assumptions similar to those used by Eyring, Hirschfelder, and Taylor (2) to explain both the radiochemical synthesis and back reaction of hydrogen bromide, but arrived at the conclusion that these results can not be explained on this basis.

The constants used for the stopping power of iodine and hydrogen iodide and for the specific ionization of iodine are more or less assumed values, because they have never been experimentally determined. Some experimentation with changes in these values indicated that the results were of the same general character, regardless of the exact values assumed for these constants. From such results it does not appear probable that the explanation of the synthesis reaction could be simplified by assuming different values for the specific ionization of iodine and the stopping power of iodine and hydrogen iodide.

SUMMARY

It has been found that the work of Vandamme and of the author, on the decomposition of hydrogen iodide by alpha particles, can be explained on the basis that 6+ molecules of hydrogen iodide decompose per hydrogen iodide ion pair.

The experiments of Vandamme and of the author on the synthesis of hydrogen iodide give data for this reaction over a range of iodine pressure from 0.3 to 350 mm. All the data can be explained on the following basis: (1) for every hydrogen ion pair 6+ molecules of hydrogen iodide are formed; (2) for every seven iodine ion pairs 1 molecule of hydrogen iodide is formed; (3) for every hydrogen iodide ion pair 4 molecules of hydrogen iodide decompose. There is a further indication, from a few of the

author's runs at very low iodine pressure, that either an appreciable back reaction takes place, or not all the hydrogen ion pairs are used up in syntheses.

The author wishes to express her thanks and appreciation to Professor S. C. Lind under whose direction this research was done, and to Professors R. S. Livingston and George Glockler for their aid and criticism in the calculation of the experimental results.

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THE IRREVERSIBILITY OF PHOTOGRAPHIC DEVELOPMENT IN ELON SOLUTIONS CONTAINING SODIUM SULFITE¹

ANGUS E. CAMERON

Kodak Research Laboratories, Rochester, New York

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In a preceding publication in this Journal (2) the writer has presented evidence that the platinum electrode potentials which R. M. Evans and W. T. Hanson, Jr., (3) of these Laboratories measured in photographic developer solutions were not oxidation-reduction potentials but were functions of the partial pressure of oxygen with which the solutions were more or less in equilibrium. The explanation given by them for the existence of an oxidation-reduction potential in the presence of sodium sulfite, which can remove the oxidized forms of photographic developer chemicals by converting them into the reduced form of the monosulfonates, was that this sulfonation process was reversible and that there was thus maintained a small and essentially constant concentration of the oxidized form of the developing agent.

Sheppard (6) and, more precisely, Beukers (1) and Reinders (5) have shown that a reversible oxidation-reduction system, such as mixtures of ferric and ferrous ions in the form of organic complexes, could act either as a reducer or as an oxidizer upon a predeveloped photographic image. Evans and Hanson have attempted to show that this is also true for organic developers in the presence of sulfite.

Within the limits of stability of the oxidized forms, some, at least, of the developer chemicals give rise to reversible oxidation reduction systems. Thus it was shown by Evans and Hanson that in solutions of amidol and oxidized amidol there was a definite reduction in density upon the high potential side of the equivalence point. However, in the presence of sodium sulfite the existence of any reversible oxidation-reduction system must be questioned. The data given by Evans and Hanson for amidol with slightly less than 1 mole of sodium sulfite per mole of reducing agent and in the presence of 8 g. of potassium bromide per liter would appear to indicate that a marked discontinuity occurred in the density-potential curve at the "equivalence" point and that the reduction in density occurring in solutions showing more positive potentials is, at best, very small.

¹ Communication No. 656 from the Kodak Research Laboratories.

Elon² was selected as the developer for the investigation reported here in order to avoid troubles caused by staining of the emulsion layer. The oxidation-reduction potential of the compound was known, as well as its "oxygen" electrode potential behavior in the presence of sodium sulfite.

EXPERIMENTAL

Motion picture positive film, No. 1301, was used for the experiments. Strips of 35-mm. film were exposed on a model 2B sensitometer, giving a series of twenty-one increasing exposures on each strip. These strips were developed for 5 minutes in D-16 (Eastman Kodak formula) at 18°C. with air agitation, rinsed in 1 per cent acetic acid, and thoroughly washed and dried in the dark. These strips were then numbered and slit lengthwise; one half of each strip was fixed in non-hardening alkaline sodium thiosulfate solution, washed, and dried. The fixed, or control strips, were then read with a Capstaff densitometer and the corresponding fixed and unfixed strips were immersed in the developer solutions for 15.5 hours with air or nitrogen agitation at 20°C. in the dark.

The glass developing tubes of half-liter capacity were jacketed and water from a 20°C. thermostat was pumped through the jackets. The film strips were suspended from the rubber stopper closing the top of the tube. Purified nitrogen or air was introduced through a perforated glass agitator tube at the bottom. A water-sealed trap permitted escape of gas from the tube. When nitrogen agitation was used, the solutions were swept out with nitrogen for an hour before the film was immersed. The nitrogen was purified by burning out the oxygen present with ammonia over a heated platinum catalyst. Ammonia was introduced by passing the gas over solid ammonium carbonate. Carbon dioxide was removed with soda lime before the gas entered the furnace tube. Excess ammonia was removed with a sulfuric acid wash.

After 15.5 hours in the developer solutions the strips were removed, washed briefly, immersed in an acid fixing and hardening bath for 5 minutes, washed thoroughly, and dried; the densities were then read on both strips. The results have been recorded as changes in density and have been plotted as a function of pH of the developer solutions. It is apparent that this is equivalent to plotting the *first* derivative of the density, and that an equivalence point of development will be shown by the reversal of sign of the change in density.

The solutions were read both before and after development with a glass electrode and platinum electrodes in atmospheres of controlled oxygen content. In many cases readings were taken with a silver electrode. The glass electrode was standardized against the hydrogen elec-

² Elon is a trade name for *p*-methylaminophenol.

trode in solutions of the same sodium-ion concentration, 1.5 *N* in all cases, in which sodium sulfite had been replaced with sodium sulfate. The buffer salt employed was, in most cases, potassium hydrogen phthalate.

TABLE 1

Results obtained with the first series of strips with nitrogen agitation
8 g. of elon, 8 g. of potassium bromide, and 6.25 g. of sodium sulfite per liter

pH	ΔD STEP 12	ΔD STEP 16	ΔD FOG	E_{air} BEFORE	E_{air} AFTER	E_{Ag}
				volts	volts	volts
3.63	-0.01	-0.01	-0.01	-0.046	-0.047	-0.080
4.18	0.01	0.00	-0.01	-0.002	-0.008	-0.082
5.20	0.05	0.04	0.01	-0.065	-0.087	-0.099
5.68	0.27	0.10	0.03	-0.092	-0.100	-0.138
6.12	0.53	0.40	0.13	-0.120	-0.144	-0.171
6.12	0.55	0.39	0.13	-0.113	-0.120	-0.180

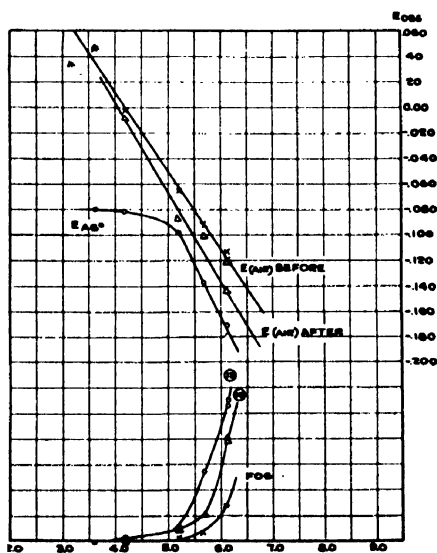


FIG. 1

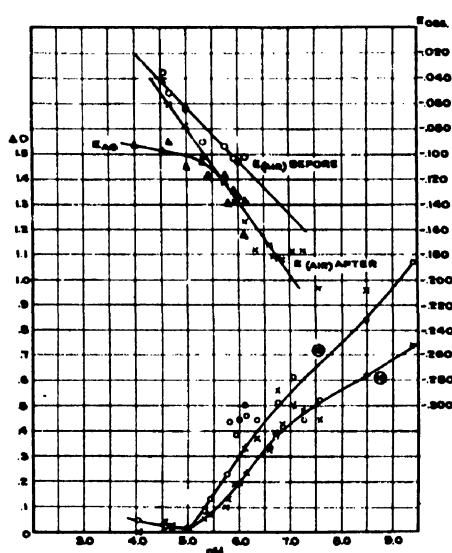


FIG. 2

FIG. 1. Change in density of predeveloped strips, and platinum and silver electrode potentials in air, as functions of the pH of the developer solution, 5 g. of elon, 8 g. of potassium bromide, and 6.25 g. of sodium sulfite per liter.

FIG. 2. Change in density of predeveloped strips, and platinum and silver electrode potentials in air, as functions of the pH of the developer solution; 8 g. of elon, 8 g. of potassium bromide, and 64 g. of sodium sulfite per liter.

Sulfuric acid was added when necessary to overcome the buffering effect of sodium sulfite in adjusting the pH to the desired value.

The 3.5 *N* calomel half-cell and bridge were used as a reference half-cell.

This combination was assigned a value of 0.2502 volt against the normal hydrogen electrode at 20°C. For convenience in comparing the results obtained and reported by Evans and Hanson, these potentials have been recorded as "observed potentials" and have not been converted to the hydrogen scale. The saturated calomel half-cell employed by Evans and Hanson is assigned a value of 0.2488 volt at 20°C.

TABLE 2

Measurements similar to those of table 1, but made with a tenfold greater concentration of sodium sulfite

8 g. of elon, 8 g. of potassium bromide, and 64 g. of sodium sulfite per liter

pH	ΔD STEP 12	ΔD STEP 16	ΔD FOG	E_{air} BEFORE	E_{air} AFTER	E_{Ag}
				volts	volts	volts
4.01	0.04	-0.01	-0.01	0.006	0.002	-0.093
4.57	0.02	0.04	0.01	-0.035	-0.041	-0.097
4.67*	0.01	0.02	-0.02	-0.052	-0.060	-0.090
5.00	0.01	0.01	0.01	-0.064	-0.077	-0.110
5.32*	0.08	0.05	0.00	-0.090	-0.102	-0.106
5.43	0.13	0.07	0.01		-0.117	-0.117
5.75	0.23	0.10	0.01	-0.094	-0.124	-0.117
5.80	0.43	0.13	0.02		-0.140	-0.139
5.93*	0.38	0.19	0.03	-0.104	-0.138	-0.129
6.00	0.44	0.19	0.03	-0.106	-0.135	-0.134
6.10	0.50	0.33	0.14		-0.165	-0.166
6.14	0.46	0.23	0.02	-0.112	-0.154	-0.138
6.35	0.44	0.37	0.35		-0.177	
6.60†	0.34	0.32	0.92		-0.173	
6.70†	0.37	0.39	1.00		-0.182	
6.75	0.51	0.56	0.50		-0.184	
6.85†	0.41	0.42	1.13		-0.184	
7.05†	0.61	0.50	2.39		-0.178	
7.25†	0.44	0.48	1.44		-0.177	
7.56	0.52	0.44	0.70		-0.207	
5.50	0.84	0.62	0.75		-0.208	-0.291
9.40	1.07	0.74	0.67		-0.240	-0.325

* Air agitation.

† Potassium dihydrogen phosphate buffer.

The first series of strips was developed in solutions of the following composition, sulfuric acid or sodium hydroxide being added as necessary to adjust the pH to the desired value: 8 g. of elon, 8 g. of potassium bromide, 6.25 g. of sodium sulfite (anhydrous), 20.2 g. of potassium acid phthalate, 106.5 g. of sodium sulfate (anhydrous), and water to make 1 liter. The results of this series with nitrogen agitation are given in table 1. These data appear graphically in figure 1, where the change in density and the

potentials are plotted as functions of the pH of the solutions. Similar measurements with a tenfold greater concentration of sodium sulfite are

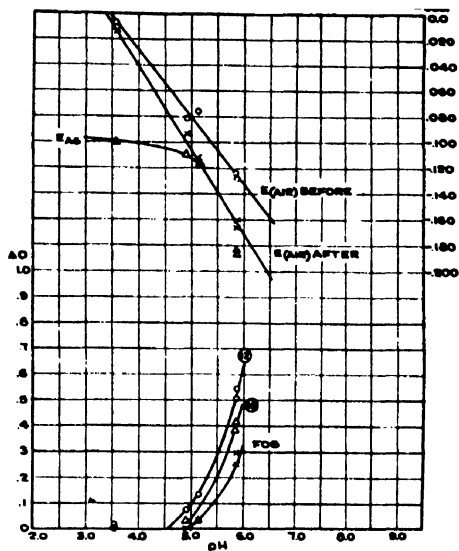


FIG. 3

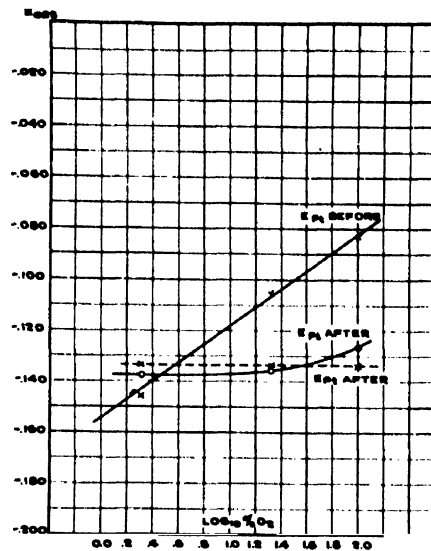


FIG. 4

FIG. 3. Change in density of predeveloped strips, and platinum and silver electrode potentials in air, as functions of the pH of the developer solution; 40 g. of elon, 8 g. of potassium bromide, and 29.2 g. of sodium sulfite per liter.

FIG. 4. Potentials of platinum and silver electrodes in air as functions of the partial pressure of oxygen at pH 6.0 in a developer containing 8 g. of elon, 8 g. of potassium bromide, and 64 g. of sodium sulfite per liter.

TABLE 3

Measurements in solutions containing five times the concentration of elon but with the ratio of elon to sodium sulfite the same as in table 1

40 g. of elon, 8 g. of potassium bromide, and 29.2 g. of sodium sulfite per liter

pH	ΔD STEP 12	ΔD STEP 16	ΔD FOG	E_{Air} BEFORE volts	E_{Air} AFTER volts	E_{Ag} volts
3.60	0.01	0.01	0.00	-0.007	-0.012	-0.100
4.93	0.07	0.03	-0.01	-0.081	-0.093	-0.108
5.15	0.13	0.03	0.03	-0.076	-0.112	-0.115
5.87	0.54	0.41	0.29	-0.128	-0.167	-0.184
5.87	0.50	0.38	0.25	-0.123	-0.161	-0.185

given in table 2. The change in fog density has been omitted from the plot of these data in figure 2 to avoid undue complication.

A third series of strips was run in solutions containing five times the

concentration of elon but with the ratio of elon to sodium sulfite mole to mole as in the data of table 1. These data are shown graphically in figure 3.

DISCUSSION

From an examination of the plotted data it is apparent that on the acid side of the pH at which development continues there is no reduction in density. Estimating this point from the plotted data and reading the potentials of the "air" electrode at the same value of pH, the data in table 4 result. None of the potentials recorded is found to be in agreement with the value of -0.150 volt given by Evans and Hanson for amidol at this bromide concentration.

The point of continuation of development is not markedly influenced by a tenfold increase in the concentration of sulfite, but a fivefold increase in the elon concentration appears to cause a shift to a lower value of pH. The measurements made with air agitation show good agreement with those made with purified nitrogen. The control strips showed slight variations in density when read for the second time. Below pH 5 there

TABLE 4

GRAMS OF ELON AND OF SODIUM SULFITE PER LITER	pH	E_{air} BEFORE	E_{air} AFTER
		volts	volts
8 g. of elon; 6.25 g. of sodium sulfite.....	5.0	-0.050	-0.062
8 g. of elon; 64 g. of sodium sulfite.....	5.0	-0.064	-0.081
40 g. of elon; 29.2 g. of sodium sulfite.....	4.8	-0.067	-0.084

were small decreases in the second densities. The first set of readings was used in determining the change of density in the predeveloped but unfixed strips.

Considerable variation appeared in the potentials of the same solution before and after development. This variation was not due to change in pH, because in every case the agreement between solutions before and after development was perfect or was within 0.05 pH unit. Figure 4 shows the behavior of the potentials before and after development as a function of the percentage of oxygen in the saturating atmosphere. The potential behavior of the platinum electrode after the film has been immersed in the solution for 15.5 hours is very much like that of a silver electrode. Kolthoff and Wang (4) have shown that gold and platinum electrodes in silver-ion concentrations greater than $0.01 M$ behave like silver electrodes and are independent of the hydrogen-ion concentration or the presence of oxygen. In low concentrations of silver ion, such as might exist in a developer solution of low reducing power in which silver has been dissolved

by the sodium sulfite, platinum electrodes show this same behavior. Solutions in which colloidal silver is present after development show a shift in the dependence of the platinum electrode potentials upon the partial pressure of oxygen. This shift to lower values of the potentials can be produced by addition of colloidal silver to a solution which has not been in contact with photographic emulsion and appears to be the result of the catalytic effect of the metal upon the rate of autoxidation of the elon. The potential dependence upon the logarithm of the partial pressure of oxygen remains a straight line.

Examination of the plots of the silver electrode potentials as functions of pH shows that the silver-ion concentration decreases above the pH at which development is found to continue. It is perhaps not surprising that such is the case, for development in solutions of such low pH, compared to those usually used in photographic development, appears to be largely, if not entirely, due to reduction of silver ion present in solution with deposition of the finely divided silver upon the nuclei present in the predeveloped image.

SUMMARY

1. Attempts have been made to determine a reversal point of photographic development in solutions of elon containing sodium sulfite.

2. A point of "continuation" of development is found which is not markedly shifted by a tenfold increase in sulfite concentration and which shows a slight shift toward lower values of pH with a fivefold increase in elon concentration.

3. The "air" electrode potential of solutions at the pH of "continuation" of development does not agree with the potential reported by Evans and Hanson for the reversal point of development in amidol solutions containing sodium sulfite.

4. It is concluded that no reversible oxidation-reduction system exists in elon solutions containing sodium sulfite.

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MEASUREMENTS OF THE IONIZATION CONSTANT OF BENZOIC ACID USING SILVER CHLORIDE ELECTRODES¹

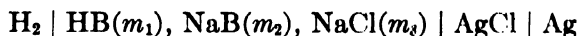
H. T. BRISCOE AND JOHN S. PEAKE

Department of Chemistry, Indiana University, Bloomington, Indiana

Received February 19, 1938

A method has been described by Harned and his coworkers for determining the ionization constants of weak acids and weak bases. In the present investigation this method has been applied to the determination of the ionization constant of benzoic acid.

Briefly, the method consists in measuring the electromotive forces of cells containing benzoic acid, sodium benzoate, and sodium chloride. These cells may be conventionally represented by



The ionization constant, K , is calculated by means of the equation:

$$E - E_0 + \frac{RT}{F} \ln \frac{m_{\text{Cl}} m_{\text{HB}}}{m_{\text{B}}} = - \frac{RT}{F} \ln K' = -RT \ln \frac{\gamma_{\text{Cl}} \gamma_{\text{HB}}}{\gamma_{\text{B}}} - \frac{RT}{F} \ln K$$

At zero ionic strength ($\mu = 0$), $\ln \frac{\gamma_{\text{Cl}} \gamma_{\text{HB}}}{\gamma_{\text{B}}}$ becomes equal to zero, so that K' then equals K . Since E , E_0 , and the molalities are measurable, K' can be determined for a number of solutions and its value at zero ionic strength be determined by extrapolation. The values of the electromotive forces of our cells and the corresponding values of the terms of the above equation are assembled in tables 1 and 2.

EXPERIMENTAL PROCEDURE

The solutions were prepared from recrystallized benzoic acid, sodium benzoate, and sodium chloride by weighing out the thoroughly dried solid reagents and adding them to weighed quantities of water.

Crystals of electrolytically deposited silver and metathetically precipitated silver chloride were used in the preparation of the silver-silver chloride electrodes. The hydrogen electrodes were prepared by the

¹ This paper is abstracted from the thesis presented by John S. Peake to the Faculty of the Graduate School of Indiana University in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

method of Hammett and Lorch. The water and hydrogen were purified in the usual manner.

TABLE 1
Composition of solutions and electromotive forces of cells

SOLUTION	m_{HB}	m_{NaCl}	m_{NaB}	μ	E
I.....	0.01636	0.01197	0.01240	0.02145	0.5785
II.....	0.01385	0.02637	0.00670	0.03320	0.5472
III.....	0.02338	0.01009	0.00480	0.03381	0.5514
IV.....	0.01858	0.02877	0.00462	0.03363	0.5294
V.....	0.01734	0.02668	0.00516	0.03204	0.5354
VI.....	0.01879	0.06823	0.00900	0.07736	0.5229

TABLE 2
Calculation of ionization constant

	n_{H}	$\frac{E - E_0}{0.05916}$	$\text{LOG } \frac{n_{\text{HB}} m_{\text{Cl}}}{m_{\text{B}}}$	$\text{LOG } K'$	$K' \times 10^5$
I....	0.00008	5.0213	-1.8065	-4.2178	6.056
II..	0.00013	5.4953	-1.2760	-4.2193	6.035
III.	0.00029	5.5662	-1.3394	-4.2268	5.932
IV..	0.00024	5.1944	-0.9643	-4.2301	5.387
V..	0.00020	5.2958	-1.0690	-4.2268	5.932
VI..	0.00013	5.0845	-0.8556	-4.2289	5.903

Extrapolated value of $K' = K = 6.05 \times 10^{-5}$

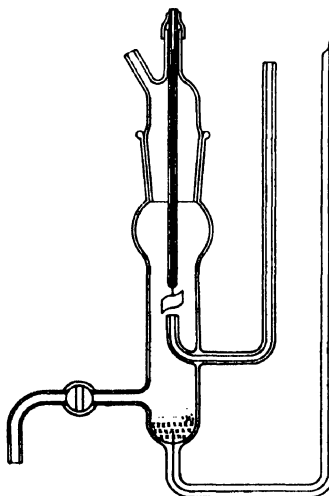


FIG. 1. The cell

The cells used in this investigation were contained in the glass vessel shown in the figure. The silver-silver chloride electrodes were placed in

the bottom of the vessel as shown, and the vessel was filled with enough solution so that the platinum foil of the hydrogen electrode was covered. The electrodes were washed repeatedly by decantation with fresh solution. This solution was first saturated with hydrogen by bubbling it through the solution before it was used for washing the electrodes or filling the cell.

During measurements the cells were kept at $25^{\circ}\text{C.} \pm 0.02^{\circ}$ by means of a thermostat, and readings were taken at 15-minute intervals until equilibrium was reached. Readings were made by means of a Leeds and Northrup Type K potentiometer and Type R reflecting galvanometer.

EXPERIMENTAL RESULTS

The values obtained for the electromotive force of cells using six solutions of benzoic acid, sodium benzoate, and sodium chloride have been listed in tables 1 and 2. Each E.M.F. value listed was obtained by comparing the values from six or more different cells containing the same solution. The molalities of the constituents of the solutions and the values of all terms of the equation for each solution are also listed in the tables. The value of E_0 is taken as 0.2221 volt.

Because of the extreme difficulty encountered in obtaining reproducible results with aqueous benzoic acid solutions in these cells, the accuracy is not claimed to be as high as that claimed by Brockman and Kilpatrick and by Saxton and Meier, who used the conductivity method. The electromotive forces were not reproducible to more than 0.1 millivolt. The difficulty in reproducibility was due chiefly to the fact that the range of acid concentrations that can be used is necessarily very small, and the activity of the hydrogen ion is limited to very low values in aqueous solutions owing to the low solubility of the acid.

This method for determining ionization constants has been found by Harned and his coworkers to yield very accurate results with acids of comparatively high solubility. The results of this investigation show that the method will also yield reasonably accurate results with the slightly soluble benzoic acid.

The value of 6.05×10^{-5} for K is slightly higher than the value of 5.9×10^{-5} obtained by Larsson from solubility measurements and lower than the values of 6.312×10^{-5} obtained by Brockman and Kilpatrick and of 6.295×10^{-5} obtained by Saxton and Meier, both from conductivity measurements. It is much lower than the value of 6.7×10^{-5} which was obtained by Kilpatrick and Chase from measurements with a quinhydrone electrode.

SUMMARY

Measurements of cells containing benzoic acid, sodium benzoate, and sodium chloride using silver-silver chloride electrodes gave a value of

6.05×10^{-5} for the ionization constant of benzoic acid in aqueous solutions.

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ELECTROKINETICS. XX. INTERFACIAL ENERGY AND THE MOLECULAR STRUCTURE OF ORGANIC COMPOUNDS. VI

THE ELECTRIC MOMENT OF ALIPHATIC ALCOHOLS, ACIDS, AND ESTERS AT CELLULOSE AND ALUMINUM OXIDE INTERFACES¹

MAX A. LAUFFER AND ROSS AIKEN GORTNER

Division of Agricultural Biochemistry, University of Minnesota, St. Paul, Minnesota

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INTRODUCTION

In previous papers in this series (3, 5) the electrokinetic properties of various solid-organic liquid interfaces were presented and discussed. In these papers, as in this one, it was assumed that the theory of Helmholtz is applicable to the electrical phenomena observed at such interfaces. The justification of this position will be presented in a subsequent paper. Using cellulose diaphragms and the streaming potential method, Martin and Gortner (5) studied the electrokinetics of a homologous series of aliphatic alcohols and of some of the substituted benzenes. Striking regularities were observed; for instance, the introduction of a methyl group into the main chain of an aliphatic alcohol changed the value of the zeta-potential by about 36 millivolts. Benzene gave no potential, and substituents in the ring influenced the zeta-potential in the order $\text{NO}_2 > \text{NH}_2 > \text{Br} > \text{Cl} > \text{CH}_3$. Jensen and Gortner (3), using the same method, studied normal fatty acids and esters at an aluminum oxide interface. Again regularities were observed within homologous series, together with an alternating effect of odd and even number of carbon atoms in the chain on electrokinetic functions. From the electric moment of the double layer and the moments of individual molecules, they calculated a function called "the percentage of 'unbalanced' orientation in the interface."

In view of the interesting relationships between electrokinetic functions and the molecular structure of organic compounds that were observed in these studies, it seemed to be desirable to extend the investigation. In-

¹ Paper No. 1594, Journal Series, Minnesota Agricultural Experiment Station. This paper is greatly condensed from a thesis presented by Max A. Lauffer, Jr., to the Graduate School of the University of Minnesota in partial fulfillment of the requirements for the degree of Doctor of Philosophy, June, 1937. The thesis containing detailed tabular data is on file in the library of the University of Minnesota.

asmuch as Martin and Gortner studied alcohols at cellulose interfaces, and Jensen and Gortner studied acids and esters at aluminum oxide interfaces, it seemed desirable to study alcohols at aluminum oxide interfaces and acids and esters at cellulose interfaces, in order to decide whether the regularities observed are fundamentally a property of the solid or of the liquid phase. This study was devoted to that task. As in the earlier studies, the streaming potential technic was used. In order to gain some insight into the mechanism of the electrical conductivity of organic liquids in diaphragms, the variations of the conductivity of methyl acetate in a cellulose diaphragm were studied with respect to temperature changes. In addition, the relationships of certain electrokinetic functions to temperature changes were also studied.

EXPERIMENTAL

Functions calculated

The electrokinetic function calculated in this study is the function introduced by Bull and Gortner (2), i.e., the electric moment of the double layer per square centimeter of surface (qd). This function imparts as much knowledge concerning the electrical properties of the interface as does the conventional zeta-potential, and it has the advantage of being free of a specific inductive capacity term and, therefore, of the hazardous assumptions concerning the magnitude of this effect in the region of the double layer. The equation presented by Bull and Gortner is,

$$qd = 2.262 \times 10^6 \frac{\eta H \kappa_s}{P} \quad (1)$$

where qd = electric moment per square centimeter expressed in electrostatic units,

η = the coefficient of viscosity,

H = the streaming potential in volts,

κ_s = the specific conductivity of the liquid in the diaphragm, and

P = the pressure in centimeters of mercury.

The values for viscosity at 30°C. used in the calculations are shown in table 1. Most of the values are interpolated from data found in the International Critical Tables. Those for *n*-butyl and *n*-amyl acetates are taken from Jensen and Gortner (3). The viscosities of *n*-amyl, *n*-hexyl, and *n*-heptyl alcohols, and of ethyl *n*-valerate, ethyl *n*-caproate, and ethyl *n*-heptylate were determined with an Ostwald viscometer.

Apparatus

The apparatus used to evaluate H/P and κ_s is a modification of the general type used in the earlier studies. In order to surmount the difficulty

of finding suitable gaskets for the earlier type of streaming potential cell, a Pyrex streaming potential cell was designed which has ground-glass joints. Figure 1 shows the new cell in detail. The compartment in which the diaphragm is packed is made by fusing together the outside parts of two 15/30 ground-glass tapers. The electrodes are made of 80-mesh platinum gauze welded onto a platinum grid, and are permanently mounted on the ends of the inside parts of the two standard tapers. Each is held in place by the tension on the platinum wire which connects it to the tungsten seal in the end of the cell.

The general apparatus was so designed that streaming potential values up to about 165 volts could be measured. This was accomplished by using a battery consisting of a variable number of dry cells in series with the potentiometer. These cells were standardized from time to time by

TABLE I
Showing the viscosity values used for the liquids studied

ORGANIC LIQUID	(η) \times 1000	ORGANIC LIQUID	(η) \times 1000
Methanol.....	5.2	<i>n</i> -Caproic acid.....	25.6
Ethanol.....	10.0	Methyl acetate.....	3.44
<i>n</i> -Propanol.....	17.6	Ethyl acetate.....	4.01
Isopropanol.....	18.0	<i>n</i> -Propyl acetate.....	5.13
<i>n</i> -Butanol.....	23.0	<i>n</i> -Butyl acetate.....	6.58
Isobutanol.....	11.37	<i>n</i> -Amyl acetate.....	7.57
<i>n</i> -Amyl alcohol.....	27.9	Ethyl formate.....	3.75
<i>n</i> -Hexanol (1-hexanol).....	37.6	Ethyl propionate.....	4.73
<i>n</i> -Heptanol (1-heptanol).....	38.4	Ethyl <i>n</i> -butyrate.....	6.04
Acetic acid.....	10.4	Methyl formate.....	3.17
Propionic acid.....	9.63	Ethyl <i>n</i> -valerate.....	7.35
<i>n</i> -Butyric acid.....	13.4	Ethyl <i>n</i> -caproate.....	9.12
<i>n</i> -Valeric acid.....	18.6	Ethyl <i>n</i> -heptylate.....	10.7

shorting their terminals through a megohm resistor and bucking a known fraction of the potential drop with a potentiometer. The E.M.F. values of the cells did not change appreciably with time.

Conductivity measurements may be made using alternating current, or, for systems of very low conductivity, using direct current. The high-resistance end of the circuit was carefully insulated with all points of contact to supports made of sulfur.

Materials

Diaphragm materials used in these studies were cellulose and aluminum oxide. The cellulose was prepared from Schleicher and Schüll filter paper No. 589, as previously described (5). Immediately before use, it was again dried in a vacuum oven at 94°C. for at least 8 hours. The aluminum oxide

was a part of the supply used by Jensen and Gortner (3). Immediately before using, it was dried in a vacuum at 94°C. for at least 8 hours. The organic liquids studied were chemicals of high quality (generally Eastman c.p. chemicals), and they were further purified by fractional distillation, end fractions being discarded and only that portion being retained which boiled in a narrow correct range.

Preparation of diaphragms

In the preparation of the cellulose diaphragms, one end of the diaphragm compartment of the streaming cell was placed over an inside taper fitted

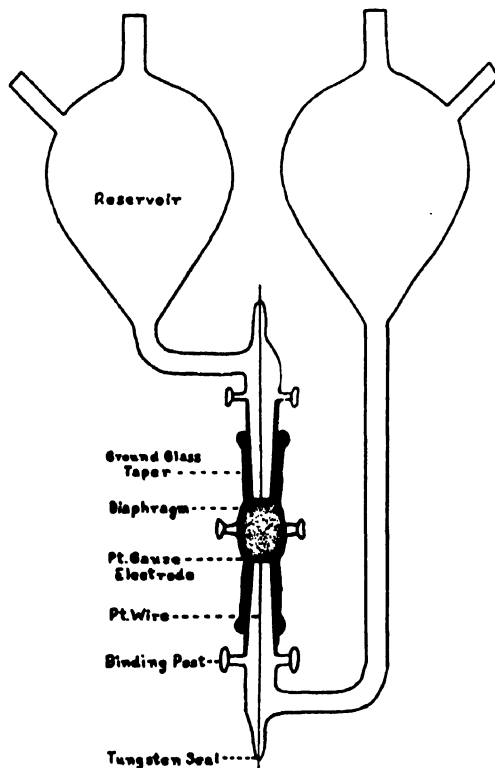


FIG. 1. Design of streaming potential cell

with a perforated gold disk on its end and permanently mounted over a heavy suction flask. Cellulose fibers, which had been soaked for at least 24 hours in the organic liquid to be studied, were then packed into the compartment, compressing with the flattened end of a stirring rod to obtain uniform packing. Excess liquid was drawn off by suction. The cell was then ready to be assembled.

A somewhat different technic was necessary in preparing the aluminum oxide diaphragms. Since the particles of aluminum oxide were small

enough to pass through the pores of the electrodes, a small cap of percale was fitted over each electrode. This cloth disk was cut with a slightly larger diameter than that of the electrode, allowing the margins to fold over the perimeter of the circular electrodes and to fit into a cylindrical groove 0.3 mm. deep and 5 mm. long, ground from the inside taper just adjacent to the electrode. Hence the cloth cap was held in place between the ground-glass walls of the inside and outside tapers, but did not prevent a tight fit of the glass joint. After one end of the diaphragm compartment was fitted to its half of the streaming cell, aluminum oxide, which had been suspended for at least 24 hours in the liquid to be studied, was packed as tightly as possible into the compartment, using suction and the flattened end of a stirring rod. The assembly of the cell was now completed. The cloth over the electrodes did not cause any appreciable error in the streaming potential, because the pressure gradient through the cloth was negligible as compared to that across the diaphragm.

Measurement of streaming potential

After the diaphragm had been packed and the streaming cell assembled, it was filled with the liquid to be studied and placed in a constant-temperature cabinet where it was allowed to remain for at least an hour before any measurements were made. Electrical contacts were made through mercury wells. The details of measurement are similar to those described in the previous papers.

In the measurement of the streaming potentials of systems with very high resistances (order of magnitude of 1000 megohms or more) the electrodes of the streaming cell were short-circuited through a high resistance (usually an 11-megohm resistor). From a practical point of view this operation lowers the probability of electrical leaks in the high-resistance end of the circuit and lowers the streaming potential which must be measured. The theoretical justification and significance of this operation will be discussed in a subsequent publication.

Measurement of specific conductivity of liquid in diaphragm

In order to determine the specific conductivity of organic liquids in the diaphragm, the conductivity in the diaphragm and the cell constant must be measured. For measurement of extremely low conductivities, the direct current circuit described by Jensen and Gortner (3) was used. The higher values of conductivity found in some systems were measured by the Wheatstone bridge principle, using an alternating current galvanometer and a 60-cycle 6-volt alternating current.

The cell constant was determined after displacing the liquid in the diaphragm by streaming 75 cc. of 95 per cent ethyl alcohol, 300 cc. of water, and finally about 100 cc. of *N*/10 potassium chloride through the dia-

phragm, and then measuring the conductivity with $N/10$ potassium chloride by the Wheatstone bridge principle. Specific conductivities of $N/10$ potassium chloride at various temperatures are taken from Reilly, Rae, and Wheeler (6). In this work the cell constant is defined as the

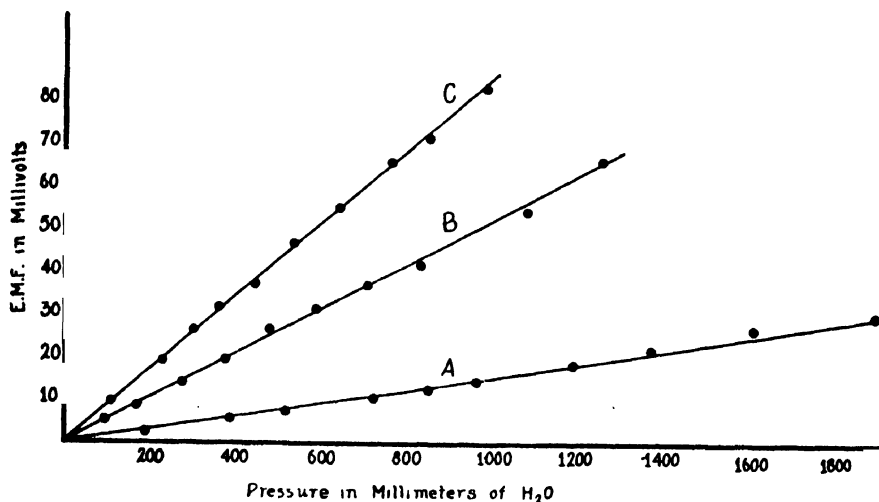


FIG. 2. Showing direct proportionality between streaming potential and hydrostatic pressure. Curve A = n -propionic acid at cellulose interface. Curve B = n -propanol at aluminum oxide interface. Curve C = ethyl n -propionate at cellulose interface.

TABLE 2

Summary of data on aliphatic alcohols at aluminum oxide interfaces at 30°C .

ALCOHOL	SIGN OF CHARGE ON Al_2O_3 SURFACE	H/P	κ_s	qd
		mv. per cm. Hg	mhos	e.s.u. per cm. $\times 10^8$
Methanol.....	—	6.82	2.73×10^{-8}	21.8
Ethanol.....	—	13.19	3.17×10^{-8}	9.42
n -Propanol.....	—	6.99	2.32×10^{-8}	6.47
Isopropanol.....	+	35.2	5.15×10^{-7}	7.36
n -Butanol.....	—	15.43	2.22×10^{-7}	1.78
Isobutanol.....	+	26.65	1.492×10^{-7}	1.02
n -Amyl alcohol.....	+	75.3	7.67×10^{-8}	3.68
n -Hexanol.....	+	123.7	1.162×10^{-7}	12.24
n -Heptanol.....	+	219.5	1.364×10^{-8}	2.60

specific conductivity of $N/10$ potassium chloride divided by the conductivity of the solution in the diaphragm. Hence the specific conductivity of the organic liquid in the diaphragm becomes its conductivity in the diaphragm multiplied by the cell constant.

The experimental data

In each system investigated from ten to fourteen independent determinations were made of the streaming potential which developed under different hydrostatic pressures. The pressures used ranged from less than 100 mm. of water to 1500-2000 mm. of water except in the cases of *n*-butyric acid,

TABLE 3

Summary of data on aliphatic acids at cellulose interfaces at 30°C.

ACID	SIGN OF CHARGE ON CELLULOSE SURFACE	<i>H/P</i>	κ_n	<i>q</i> ^d
		<i>mv. per cm. Hg</i>	<i>mhos</i> $\times 10^3$	<i>e.s.u. per cm. $\times 10^8$</i>
Acetic acid.....	+	21.4	1.732	8.74
Propionic acid.....	+	2.10	2.43	1.12
<i>n</i> -Butyric acid.....	—	0.457	2.49	0.345
<i>n</i> -Valeric acid.....	—	0.780	2.365	0.773
<i>n</i> -Caproic acid.....	—	0.996	2.42	1.40

TABLE 4

Summary of data on aliphatic esters at cellulose interfaces at 30°C., using an 11-megohm shunt

ESTER	SIGN OF CHARGE ON CELLULOSE SURFACE	<i>H/P</i>	κ_n	<i>q</i> ^d
		<i>mv. per cm. Hg</i>	<i>mhos</i> $\times 10^3$	<i>e.s.u. per cm. $\times 10^8$</i>
Methyl acetate.....	—	56.9	3.07	13.65
Ethyl acetate.....	—	24.3	2.595	5.72
<i>n</i> -Propyl acetate.....	—	11.05	2.45	3.13
<i>n</i> -Butyl acetate.....	—	10.7	2.30	3.67
<i>n</i> -Amyl acetate.....	—	5.17	2.385	2.105
Ethyl formate.....	—	48.7	2.855	11.80
Ethyl propionate.....	—	1.51	2.445	3.02
Ethyl <i>n</i> -butyrate.....	—	8.80	2.365	2.85
Methyl formate.....	—	113.8	2.72	22.3
Ethyl <i>n</i> -valerate.....	—	9.60	2.95	4.71
Ethyl <i>n</i> -caproate.....	—	7.05	3.66	5.33
Ethyl <i>n</i> -heptylate.....	—	5.69	3.00	4.14

n-valeric acid, and *n*-caproic acid, where pressures ranging from 40 to 850 mm. of mercury were employed. Typical series of data are shown in figure 2, where the E.M.F. developed is plotted against the pressure of streaming. Curve A is for *n*-propionic acid and curve C for ethyl propionate at cellulose interfaces. Curve B is for *n*-propanol at an aluminum oxide interface. In all cases the data could be fitted to a straight line

passing through the point of origin. Accordingly H was found to be proportional to P for all studies reported in this paper. This agrees with the earlier studies and is an essential requirement if the theory of Helmholtz is to be applied to organic liquids at interfaces.

Since the ratio H/P was found to be a constant, the individual measurements are not presented in detail; summaries are given in tables 2, 3, 4, and 5. In these tables the value H/P is taken to be the slope of the line which best fits the points obtained by plotting H against P , as is illustrated in figure 2. In some instances the function κ'_s is reported instead of κ_s . This function is defined as the conductivity of the system, diaphragm in parallel with shunt, multiplied by the cell constant of the diaphragm.

TABLE 5

Summary of data on effect of temperature on a methyl acetate-cellulose interface

TEMPERATURE	H/P	κ_s	$H\kappa_s/P$
°C.	mv. per cm. Hg	mhos $\times 10^8$	$\times 10^8$
40	522	3.82	20.0
35	498	3.67	18.27
30	488	3.41	16.67
26.8	492	3.245	16.0
21	501	2.905	14.58

DISCUSSION

We have noted that for all of our series of data the plot of H/P was essentially a straight line passing through the point of origin. Martin and Gortner (5) and Martin (4) found a change of the function, zeta, with pressure for certain alcohols at cellulose interfaces. In their studies a value of zeta was calculated for every observation of pressure and potential, using the equation,

$$\zeta = \frac{4\pi H\kappa_s\eta}{P\epsilon} \quad (2)$$

In the cases of methanol and isopropanol (2-propanol) zeta changed rapidly when pressure was varied in the low pressure range, while little or no change of zeta took place with changes of pressure at higher values of P . In the ethanol-water-cellulose system, a reversal in the sign of zeta was reported for low values of P . (The system described as ethanol-water-cellulose was a system the liquid phase of which was water, the solid phase being cellulose which had been in contact with ethanol before water was introduced into the cell.) Isobutanol (2-methyl-1-propanol) at a cellulose interface showed this effect to a smaller degree than did isopro-

panol or methanol. Ethanol, 1-propanol, and 1-butanol showed the effect to only a very slight degree.

In figure 3, H is plotted against P for Martin's data on (A) methyl alcohol, (B) ethanol, (C) ethanol-water, (D) n -propanol (1-propanol), (E) isopropanol, (F) n -butanol (1-butanol), and (G) isobutanol at cellulose interfaces. An inspection of this figure shows that the data for all of these systems fall on essentially straight lines. The curves fail to pass

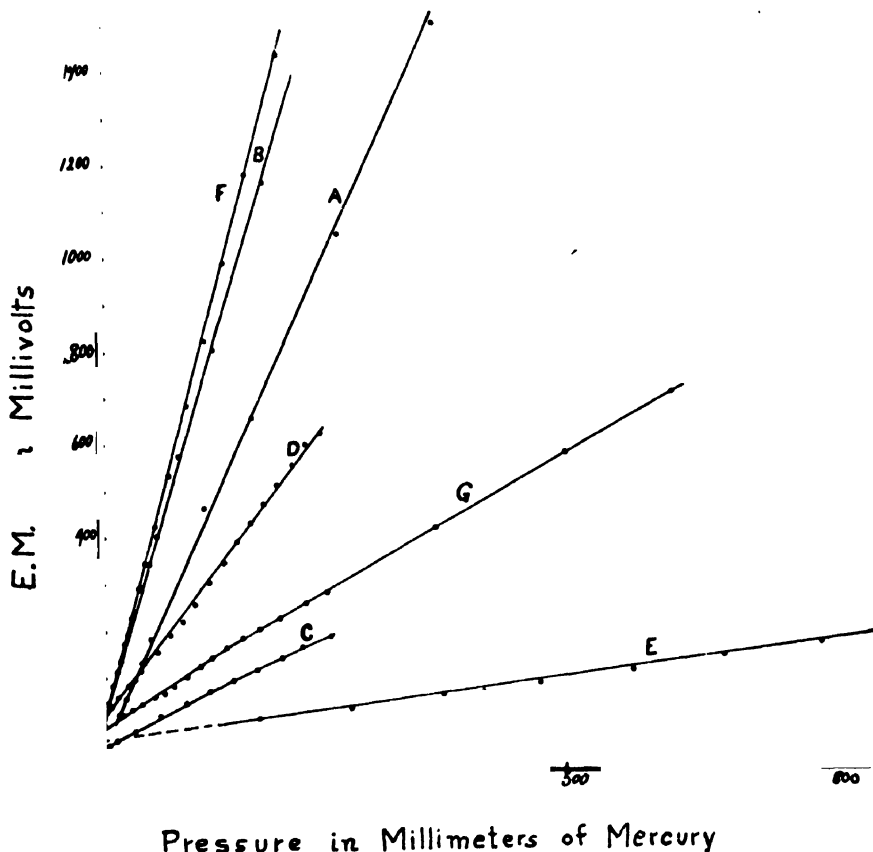


FIG. 3. Data of Martin and of Martin and Gortner for a variety of alcohols at a cellulose interface (for description see text).

through the origin by a considerable margin in the cases of methanol, isopropanol, and ethanol-water, fail by a small margin in the case of isobutanol, and practically pass through it in the cases of ethanol, n -propanol, and n -butanol. It is seen, then, that the zeta-pressure effect that he reports parallels the extent to which the H/P curves fail to pass through the origin of coördinates. It is possible to explain this failure of some of the curves to pass through the origin by assuming that an erroneous value

for the zero point of the electrometer had been used. Such a mistake could easily be made if the zero point were taken to be the position of the electrometer needle when the circuit is open.

The behavior of organic liquids at interfaces

Figure 4 shows the way in which the electric moment of the double layer at aluminum oxide interfaces varies from alcohol to alcohol as one builds

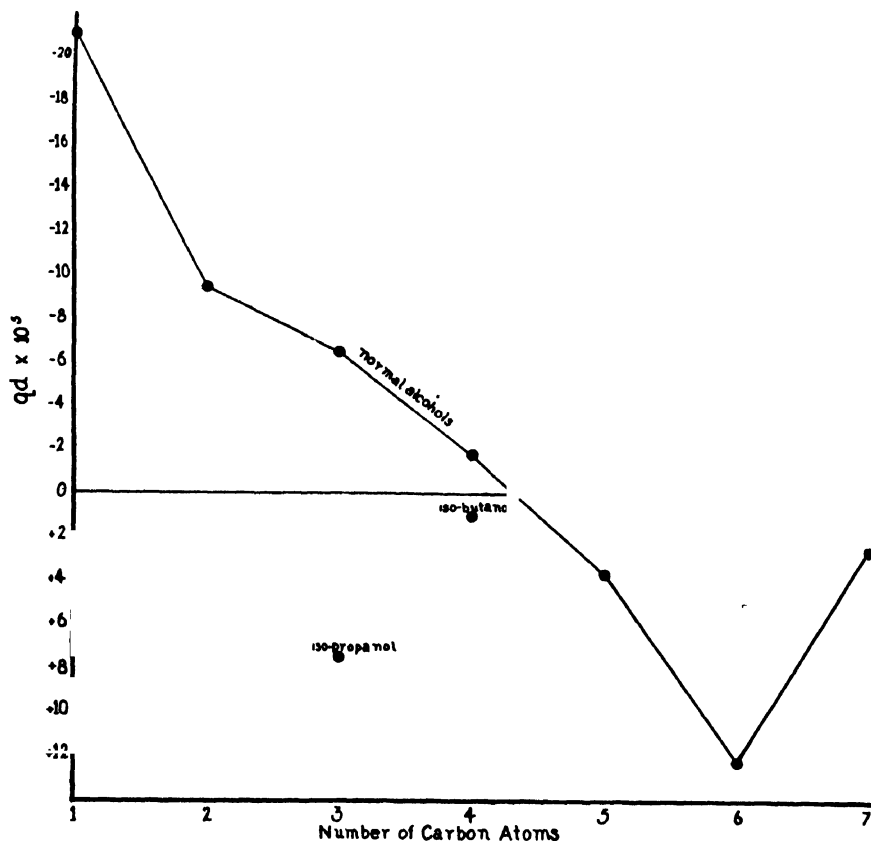


FIG. 4. The variation in the electric moment at an alcohol-aluminum oxide interface plotted as a function of the number of carbon atoms in the alcohol molecule.

up the length of the carbon chain. Figure 5 contains the data of Martin and Gortner (5) for the same alcohols recalculated to show the same relationship at a cellulose interface. They considered their data for *n*-pentanol of doubtful value, since *n*-pentanol of unquestioned purity was not available at the time they made their determinations. The magnitudes of the electric moments are about twice as great for alcohols at cellulose interfaces as they are for alcohols at aluminum oxide interfaces.

Figure 6 shows the variation of the electric moment of the double layer

at cellulose-fatty acid interfaces as one increases the number of carbons in the chains of the simple fatty acids. The relationship is quite regular. It will be noticed that there is a reversal of the sign of the charge on the

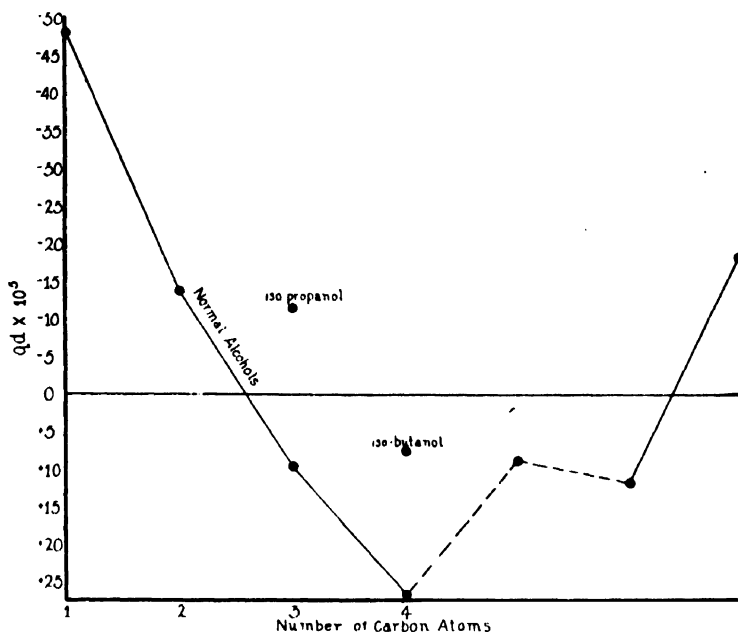


FIG. 5. Data similar to those in figure 4 except for an alcohol-cellulose interface (plotted from recalculated data of Martin and Gortner).

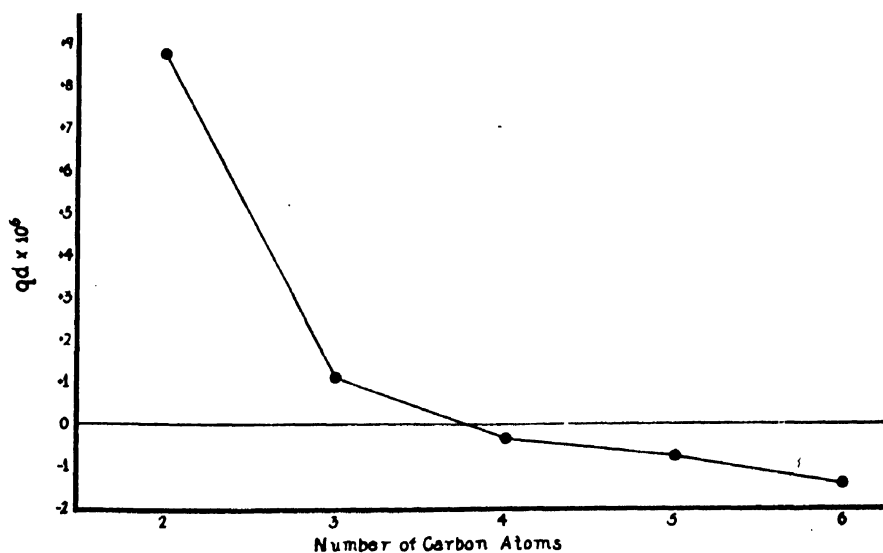


FIG. 6. The electric moment at a fatty acid-cellulose interface plotted as a function of the number of carbon atoms in the normal acid.

surface when one goes from three to four carbon atoms in the chain of the acids. Jensen and Gortner (3) found values for qd for the same acids at aluminum oxide interfaces that are about ten times as large as these values at a cellulose interface. Furthermore, in all of their studies with acids the sign of the charge on the surface of the solid was found to be positive.

In figure 7 we find the electric moments of esters at cellulose interfaces shown in relation to the number of carbon atoms in the chain of the ester. The unbroken line (A) connects points which represent the electric moments of double layers of the esters of acetic acid at the cellulose interface,

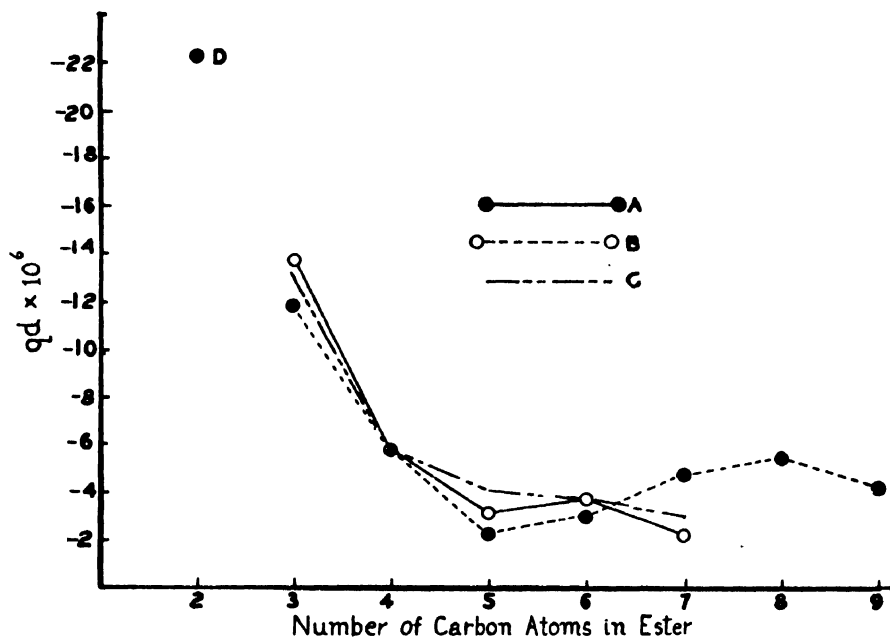


FIG. 7. The electric moment of a series of aliphatic esters at a cellulose interface plotted as a function of the number of carbon atoms in the ester. A = esters of acetic acid; B = esters of ethyl alcohol; C = the curve in figure 6 somewhat displaced with reference to coordinates to indicate similarity (see text); D = electric moment of methyl formate.

whereas the broken line (B) connects points which represent the electric moments of the esters of ethyl alcohol. Point D is the moment for methyl formate at a cellulose interface. In a crude way the electrical properties of esters at cellulose interfaces seem to be related to the number of carbon atoms in the chain of the esters. The broken line (C) was copied from the line joining the points in figure 6 with the sign ignored, displaced the distance of one carbon atom to the right on the horizontal axis, and displaced somewhat along the vertical axis. However, no distortion of the shape of the curve was made. This curve was drawn in figure 7 in order to show the striking similarity between the actual magni-

tude of the variations in electric moment of the double layer at cellulose interfaces as one ascends homologous series of acids on the one hand, and esters on the other hand. The data of Jensen and Gortner (3) for the same esters at aluminum oxide interfaces show negative surfaces, with the exception of ethyl formate, which is positive. Methyl formate, ethyl valerate, ethyl caproate, and ethyl heptylate were not included in their study. The values of the moments for the systems which they studied are about three times as great as are the ones reported for esters in this study. Their data show no similarities between the ethyl alcohol series of esters and the acetic acid series.

Figure 8 shows the way in which the conductivity of methyl acetate in a cellulose diaphragm and the electrokinetic function, $H\kappa_s/P$, measured for

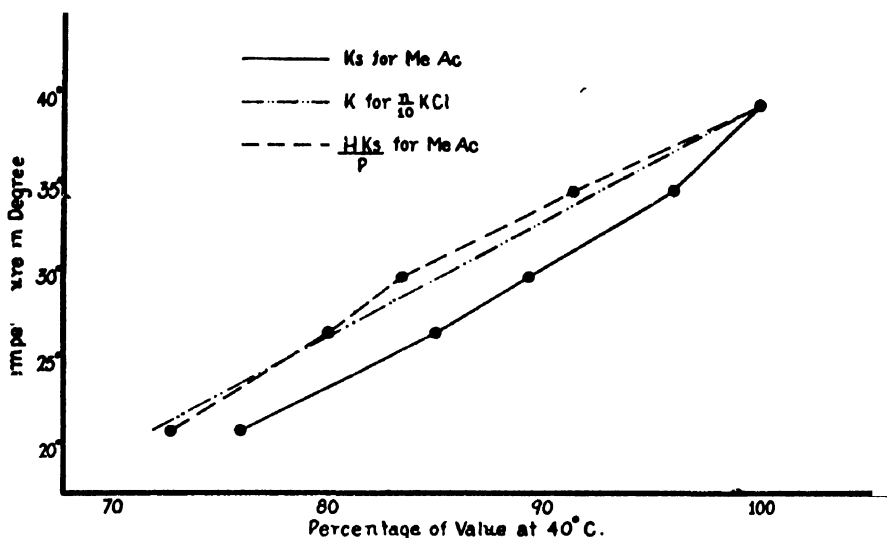


FIG. 8. Showing temperature effects upon the conductivity and electrokinetic functions in a methyl acetate-cellulose diaphragm.

that system, vary with temperature. The values shown are plotted as the percentage of the values at 40°C. The variation of the specific conductivity of $N/10$ potassium chloride with temperature is included in the figure in order to point out the similarity between the temperature coefficient for the conductivity of potassium chloride and that for the conductivity of methyl acetate in the diaphragm.

These temperature coefficient studies were made in order to obtain some idea of the means by which electric currents are conducted by organic liquids in diaphragms. Conductivity can be either ionic or electronic. The former has a positive temperature coefficient, while the latter has a negative temperature coefficient. The behavior of the conductivity of methyl acetate with changing temperature, as well as the results

of the similar study made by Bull and Gortner (1) on the system ethyl alcohol-cellulose, points strongly to the conclusion that ions are responsible for the conductivities shown by organic liquids in the diaphragms under consideration. The possible origin of the ions is problematical. It is possible that when a molecule of an organic compound orients itself in the region of an electrical center on the surface of the solid, an inductive effect takes place within either the oriented molecule or the configuration of atoms constituting the surface. This might cause a valence bond holding a proton, in one case, or a hydroxyl group, in the other, to be weakened, permitting a slight ionization at the interface. This could account for the presence of a charge on the surface, which is negative for some systems, and positive for others. It would also afford the ions necessary for the conductivity measured, and would give us some reasonable mechanism for the building up of the streaming potentials observed in these systems.

An alternative hypothesis would be the presence in the organic liquid (e.g., alcohols) of both "alcoholate" and "alcoholonium" ions. If the "alcoholate" ion is more strongly adsorbed than is the "alcoholonium" ion, then the solid will be negatively charged with respect to the streaming liquid, with a reversal in charge resulting whenever the adsorption of the "alcoholonium" ion exceeds that of the "alcoholate" ion. This appears to us to be the more probable mechanism. It is, however, difficult to explain why cellulose adsorbs preferentially the alcoholonium ion of *n*-propanol and the alcoholate ion of isopropanol and why these adsorption affinities are reversed when the cellulose is replaced by aluminum oxide. In the case of cellulose both *n*-butanol and isobutanol induce the same sign of charge at the interface, whereas opposite charges are induced at an aluminum oxide interface. Furthermore the physicochemical constants of the aliphatic acids afford no clue as to why a reversal in interfacial sign occurs as we pass from *n*-propionic acid to *n*-butyric acid at a cellulose-acid interface, whereas no similar reversal occurs at an aluminum oxide-acid interface. In some way these electric moments at the interface appear to be reflecting not only the interatomic structure of the organic liquids but also the interatomic, or at least the surface-atomic structure of the solid which is bathed by the organic liquid. Since the data obtained are easily reproducible, and since they cannot be predicted *a priori* from any existing physicochemical data, they afford an independent method for the study of the relationships which exist between organic structure and surface behavior.

SUMMARY

The electric moment of the double layer per square centimeter (qd) was determined for an homologous series of the aliphatic alcohols at aluminum oxide interfaces and for similar series of the fatty acids and esters at cel-

lulose interfaces, using the streaming potential method. A new streaming cell with ground-glass joints was designed and used throughout these studies. This cell markedly increases the ease with which measurements can be made. In order to obviate the difficulties encountered in dealing with diaphragms of extremely high resistance and with the measurement of streaming potentials of excessively large magnitude, the electrodes of such diaphragms were shunted through an 11-megohm resistor, thus adding a new technic to electrokinetic methods. The data lead to the following conclusions:

1. The streaming potential was strictly proportional to pressure for all of the systems investigated.

2. At aluminum oxide interfaces alcohols, within an homologous series, show variations of electrokinetic functions which resemble to a considerable extent the variations at cellulose interfaces. The electric moment (qd) of alcohols at aluminum oxide interfaces are in general about half as large as are those at cellulose interfaces.

3. A reversal from (-) to (+) occurs between *n*-butanol and *n*-pentanol at an aluminum oxide interface and between ethanol and *n*-propanol at a cellulose interface. In both series isopropanol yields a sign opposite to that yielded by *n*-propanol.

4. Fatty acids at cellulose interfaces show a reversal of sign of surface charge between *n*-propionic acid and *n*-butyric acid. No such reversal is shown at an aluminum oxide interface. The magnitudes of qd are about one-tenth of those of acids at aluminum oxide interfaces.

5. Within an homologous series of esters the variations in electric moments at cellulose-ester interfaces seem to be closely associated with the number of carbon atoms in the ester. The variations, though opposite in direction, are of approximately the same magnitudes as the variations at cellulose interfaces encountered in ascending the homologous series of fatty acids. Furthermore, the behavior of an ester is analogous to that of the fatty acid containing one less carbon atom. Moments for esters at cellulose interfaces are about one-third as great as are those for esters at aluminum oxide interfaces.

6. Specific effects of surfaces on the electrical behavior of types of compounds must be postulated in order to rationalize the findings of this study with the earlier data of Martin and Gortner and of Jensen and Gortner.

7. Positive temperature coefficients of the conductivity of methyl acetate in the diaphragm and of $H\kappa_s/P$ for the same system were observed. It is postulated that the electrokinetic effects observed are the resultant of the interaction of ions derived from the organic molecules of the liquids and the solid with which the liquid is in contact.

8. Since the electrokinetic behavior of a solid-organic liquid interface cannot be predicted *a priori* from existing physicochemical data, it is sug-

gested that electrokinetic studies afford an independent technic for studying problems of organic chemistry.

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A PHYSICOCHEMICAL STUDY OF BLOOD SERA. III
COLLOID OSMOTIC PRESSURE. AN ANALYSIS OF ONE HUNDRED CASES

JOSÉ ZOZAYA

Gladwyne Research Laboratories, Gladwyne, Pennsylvania

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The importance of the colloid osmotic pressure of the blood proteins in the interchange of fluids in the body is generally recognized. Since the work of Starling (14) a great many investigators have studied the colloid osmotic pressure of blood serum or plasma. These investigators have used different techniques, with variations in the conditions observed, such as temperature, concentration of serum, pH, different bathing fluids, and many kinds of membranes, all of which influence the final result. Few of these workers have used a theoretical colloid osmotic pressure value which could be calculated from the molecular weight of the serum proteins by the formula RTC/M , where C is the protein concentration and M the molecular weight of the protein.

The literature on the determination of the colloid osmotic pressure of human serum is large. For our present consideration we are interested mainly in the actual values obtained by different workers, so we have used the table given by Drinker and Field (4) and have determined the average values from the list given by them. These will be discussed later. The bibliography is given by Drinker.

Colloid osmotic pressure measurements were used in the first determinations of the molecular weight of serum albumin in a well-defined composition by Sørensen (13), who obtained the value of 45,000. By a similar method Adair (2) found the value to be 62,000, but he made some modifications in the calculations. Svedberg and Sjögren (15), using the ultracentrifuge, found the molecular weight of serum albumin to be 68,000 and that of globulin 169,000. In further work with the colloid osmotic pressure method, Adair (3) found the new values 72,000 for serum albumin and 170,000 for globulin. These last figures are the ones used in our calculations. It is of interest to note the close agreement between the values obtained by the different methods.

There are many factors which influence the colloid osmotic pressure of protein systems, such as the Donnan effect, the pressure due to the diffusible ion, etc., but they become of greater interest in academic studies with

perfectly controlled systems. The important physiological consideration is the constant and accurate measurement of the colloid osmotic pressure of the blood serum as is, for it is in this form that the important physiological effect is obtained. In this work we shall not discuss the probable factors influencing our determinations other than those mentioned, for they already take into consideration the optimum conditions for eliminating some of the effects.

Adair (3) studied the serum albumin and globulin separately and in the whole serum, and he concluded that their behavior, so far as colloid osmotic pressure is concerned, follows Dalton's law of partial pressures and that it appears that serum protein is not a compound of albumin and globulins. He further believes that the state of aggregation of the proteins in the untreated serum appears to be the same as their state of aggregation in the purified proteins. With these experimental facts, we studied one hundred samples of human serum (from mental and nervous cases), only one showing a marked alteration. (This was sample No. 88, from a case with *granuloma inguinale*, which had a total protein of 10.75 and an A/G of 0.77.) The colloid osmotic pressures determined experimentally were compared with the theoretical values calculated on the basis of the added effects which the amount of serum albumin and globulin produced, their molecular weights in an ideal solution being considered.

METHODS

The general technique which we followed is essentially that described by Adair (1) in his studies on the molecular weight of hemoglobin. A detailed description of the method is given below.

Collodion membranes

A 2 per cent parlodion (Pyroxylin Purified, Mallinckrodt) solution was made with equal parts of ether (distilled over sodium) and absolute alcohol. To this solution was added sufficient ethylene glycol to make a final concentration of 2 per cent. The percentage of ethylene glycol affects the permeability of the membrane, which increases with the percentage of the glycol. In our experience we found that a 2 per cent concentration gave the ideal permeability. It is best to let the solution of collodion rest for at least two weeks before using it. On a revolving glass tube, 1.1 cm. in diameter, arranged in a rotary mechanical device, the collodion was poured on at least 4 cm. of the length of the tube, including the end. After 1.5 minutes a second coating of collodion was applied. This procedure was repeated four times with 1.5-minute intervals between each pouring. After the fourth coating, 6 minutes were allowed to pass before shutting off the motion of the tube and the heat. Then the tube was allowed to dry overnight before the membrane was removed. An important provision is to have a heater two feet in front of the tube, while the

collodion is being poured, to hasten drying. Before use all membranes were submitted to a pressure of 2.5 atmospheres with a mercury pump, to test their permeability and strength.

Osmometer

A heavy glass tube with a thin capillary opening graduated in millimeters was used as the osmometer (Westergren sedimentation tube). The details of the arrangement are best seen in figure 1, where A is the vacuum of a thermos bottle, B the collodion sac of 2-cc. capacity, which is fitted tightly to a rubber stopper D by means of a fine rubber thread C. Inserted through the stopper is a thin glass tube E, which by means of a

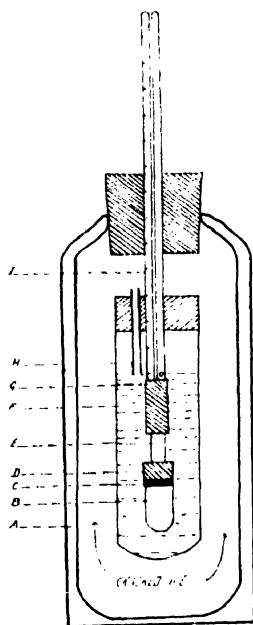


FIG. 1. Osmometer apparatus in thermos

rubber tube G connects the osmometer I with the collodion bag. The bag containing the serum is immersed in a large test tube through a stopper, which has a small glass tube inserted on the side to enable it to touch the surface of the bathing liquid. Both should be at the level of the zero surface of the osmometer. The tube prevents pressure on the liquid when the stopper is tightly fitted to the tube. The whole apparatus is immersed in a thermos bottle which has previously been filled with finely cracked ice, a space being formed in the ice for the tube to fit into it. To keep a constant temperature of 0°C. the bottle was refilled with ice every other day, for low temperature is the most important factor in insuring chemical stability.

Bathing fluid

The bathing fluid used in these experiments was an equal mixture of Sørensen's disodium hydrogen phosphate and potassium dihydrogen phosphate in $M/30$ concentration. With the use of this low concentration of salts, the Donnan effect is negligible and no correction is made in our calculations. Further experiments are being made to measure the partial osmotic pressure of the protein ions. The pH at room temperature (18°C.) was 6.81 and at 0°C. was 6.91. The solution in the tube was changed daily at the time of the reading of the manometer. A constant pH of the fluid in colloid osmotic pressure determinations is of importance, for we know that it has an effect on the colloid osmotic pressure of proteins.

Calculations

$$p = R_1 - (R_2 - R_3) \frac{\text{Sp. G.}}{13.6}$$

R_1 = the scale reading of the meniscus on the osmometer,

$R_2 - R_3$ = the difference in the meniscus reading when the tube is dipped in the tube of the inner liquid (capillarity), and

Sp.G. = the specific gravity of the serum.

Readings of the manometer were made every day until an identical reading was observed for two or three consecutive days, when it was thought that equilibrium had been reached. All results are expressed in millimeters of mercury and at 0°C.

The theoretical calculation of colloid osmotic pressure was determined by the formula

$$p = \frac{RT(10C_a)}{M_a} + \frac{RT(10C_g)}{M_g}$$

where $RT = 760 \times 22.412 = 17,033$ at 0°C.,

M_a = molecular weight of serum albumin (72,000),

M_g = molecular weight of serum globulin (170,000),

C_a = concentration of albumin in the serum (per cent), and

C_g = concentration of globulin in the serum (per cent).

The concentration of the proteins is multiplied by 10 to make the relation in terms of parts per thousand.

The theoretical colloid osmotic pressure per gram of protein is denoted by n_0 in comparison to n , which is the relation of the colloid osmotic pressure determined per gram of protein. The value of n_0 was experimentally determined by Adair (3) as 2.36 for albumin and 1.00 for globulin. He also determined it in unfractionated serum and found it to be 1.90 ± 0.2 . Using the data published by Verney (16), Mayrs (10), and Marrack and Hewitt (9), and recalculating their values to millimeters of mercury and for 0°C., Adair found 1.8 ± 0.2 , 1.89 ± 0.2 , and 1.9 ± 0.2 , respectively.

The determined value for n_0 in the serum studied by Adair was 1.94, which agrees with the theoretical one within the limits of experimental error. From the values obtained for albumin and globulin one can calculate the theoretical value for n_0 for any given serum by taking into consideration the relative percentages of each fraction in the whole serum.

The ratio $p/RTCp$ is the relation of the observed colloid osmotic pressure and the calculated one.

Other measurements

The determination of the specific gravity and the relative viscosity as well as the fractionation of the proteins have already been described in a previous paper (18).

Time of observation

In the present series the average time for a serum to come to equilibrium was 10 days, the shortest time being 6 days, and the longest 32 days. (This extreme was a serum with a total protein of 10.75 and an A/G of 0.77.)

RESULTS

For lack of space the complete data on the one hundred cases cannot be published, so they have been tabulated in the form of general averages (table 1), showing the maximum and the minimum in each measurement to give an idea of the range of variation.

Our first consideration was to compare the theoretical and observed colloid osmotic pressures. In the total averages we find a difference of 1.24 mm. of mercury (1.78 cm. of water), or a difference of 9.4 per cent. Besides this discrepancy the colloid osmotic pressure reading has to account for the corrections in the probable error in the determination of the protein fractions, etc. We made only one determination of each one of the sera. One must consider also the correction of the volume occupied by the proteins, ion-pressure differences in non-ideal solutions, the volume occupied by the protein molecules, that is, the b in van der Waals equation, and other technical corrections, which were not taken into consideration. So we consider that the agreement between these two values is very good.

The ratio $p/RTCp$ in the general average is 0.906. The minimum 0.70 was from a serum with a total protein of 10.75 and an A/G of 0.77, a specific gravity of 1.0352, and a viscosity of 2.59, a definitely abnormal serum. The maximum, which should be 1.00, was found to be 1.07 in a serum with a total protein of 6.04 per cent and an A/G of 2.45, probably opposite to the one above. It may be suggested that probably the general average would be higher if some of these abnormal sera had been eliminated from our general consideration. But it is of importance to know how these kinds of sera behave.

The literature on colloid osmotic pressure determinations on human serum is very extensive, as has already been noted in the introduction, so the results of our averages were determined from Drinker's table. The colloid osmotic pressure was 33.25 cm. of water or 24.44 mm. of mercury. No correction was made for the temperature. The total protein in the average was 7.76 per cent, and the number of cases studied was three hundred and ninety-four. The value of n would be 3.02 mm. of mercury, compared to 1.702 in our cases. We are not able to explain these differences, the figures given by Drinker and Field being so much higher, nor can we correlate their findings with the theoretical expectation when taking into consideration the molecular weights of serum albumin and globulin.

These high values for the colloid osmotic pressure of human serum as found by other investigators have made the understanding of the water

TABLE 1

Total average with maxima and minima of the various calculations on one hundred sera

	SPECIFIC GRAVITY	VISCOSITY	TOTAL PROTEIN	ALBUMIN	GLOBULIN	ALBUMIN GLOBULIN	p^*	$RTCp$	n	n_0	$p/RTCp$
Maximum....	1.0358	2.59	10.75	5.64	6.06	3.76	13.53	16.98	2.11	2.07	1.070
Average.....	1.02717	1.776	7.037	4.525	2.512	1.801	11.96	13.201	1.702	1.876	0.906
Minimum.....	1.0240	1.61	5.50	2.93	1.48	0.71	8.51	9.46	1.04	1.56	0.695

* p = observed colloid osmotic pressure in millimeters of mercury.

$RTCp$ = calculated colloid osmotic pressure from formula 1.

n = colloid osmotic pressure per gram of protein (determined).

n_0 = colloid osmotic pressure per gram of protein (theoretical).

interchange rather difficult, and several hypotheses have been advanced to explain this fact, mainly those of Krogh (7), Schade (12), and Landis (8). Krogh and his coworkers could not detect any accumulation of fluid in the tissues until the obstructing pressure exceeded 15 mm. of mercury. They concluded that this represented a critical pressure below which there was no gross disturbance of the fluid balance between blood and tissues. It is of interest to note that our highest colloid osmotic pressure observed was 13.54 mm. of mercury, which is below the critical pressure observed by them. In another paper we shall discuss this point further.

Govaerts (6), who studied the colloid osmotic pressure of human serum extensively and whose results are generally quoted in the literature, found that 1 g. of serum albumin exerted a pressure of 5.5 mm. of mercury and 1 g. of globulin a pressure of 1.4 mm. of mercury. From these findings

he suggested the calculation of the colloid osmotic pressure of a serum from the A/G , and he thinks that there is an approximation of within 10 per cent. We have plotted the A/G and our value n in figure 2. We can see the wide distribution of our findings away from the theoretical line. So it is difficult to imagine any close agreement by calculating colloid osmotic pressure from these data. At the same time it would be inadvisable to calculate any colloid osmotic pressure of any serum from standardized formulas, for one would not be able to detect those sera which

TABLE 2

Group of cases showing the same values of A/G and n_0 , with different values of n and $p/RTCp$

CASE NO.	SPECIFIC GRAVITY	VISCOSITY	TOTAL PROTEIN	ALBUMIN GLOBULIN	n	n_0	$p/RTCp$
3.....	1.0274	1.75	7.58	2.05	1.68	1.91	0.88
4.....	1.0254	1.65	6.81	2.02	1.80	1.91	0.94
19.....	1.0277	1.79	7.03	2.00	1.92	1.91	1.00
20.....	1.0273	1.75	7.03	2.00	1.80	1.91	0.94
25.....	1.0258	1.61	6.59	2.03	1.85	1.91	0.97
31.....	1.0246	1.64	5.83	2.00	1.72	1.91	0.90
39.....	1.0265	1.69	6.16	2.05	1.73	1.91	0.91
62.....	1.0271	1.73	6.59	2.03	1.56	1.91	0.94
73.....	1.0261	1.68	6.37	2.05	1.92	1.91	1.00
84.....	1.0289	1.90	8.23	2.02	1.51	1.91	0.79

TABLE 3

Group of cases showing a value for n of 1.80

CASE NO.	SPECIFIC GRAVITY	VISCOSITY	TOTAL PROTEIN	ALBUMIN GLOBULIN	n_0	$p/RTCp$
4.....	1.0254	1.65	6.81	2.02	1.91	0.94
20.....	1.0273	1.75	7.03	2.00	1.91	0.94
34.....	1.0247	1.64	6.59	1.71	1.85	0.97
47.....	1.0251	1.69	6.59	1.31	1.79	1.01
48.....	1.0273	1.74	6.92	2.54	1.97	0.91
70.....	1.0260	1.68	6.70	1.78	1.87	0.96
72.....	1.0248	1.65	6.05	2.71	1.99	0.81
81.....	1.0260	1.69	6.92	2.10	1.92	0.94

behave differently owing to radical changes in the behavior of the molecules because of some disease condition.

To study further differences in sera besides the A/G , we selected a group of cases which had the same total protein per cent (table 4) and observed the variations in the other measurements. The value of A/G ranged from 1.31 to 2.46, the value of n from 1.56 to 1.96, and the ratio $p/RTCp$ from 0.85 to 1.01, showing that the concentration of the protein in itself had no direct effect on the value of n .

We then studied the group of cases with a $p/RTCp$ of less than 0.85 (table 5), and noticed that the total concentration of the protein ranged from 6.05 per cent to 10.75 per cent, the A/G from 0.77 to 2.81, and the value of n from 1.09 to 1.67, with nothing characteristic to explain the low ratio. Then we selected a group of cases which showed a value for

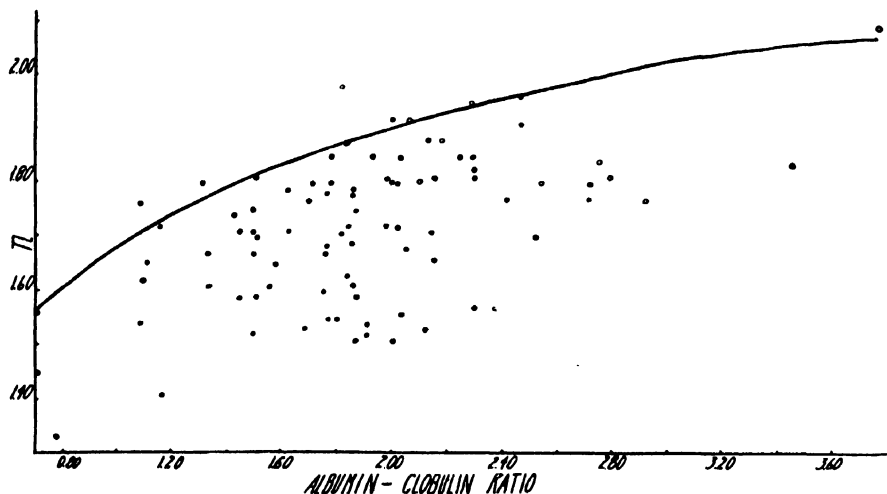


FIG. 2. Relation of albumin-globulin ratio to osmotic pressure per gram of protein

TABLE 4

Group of cases showing the same total protein and different values of n and $p/RTCp$

CASE NO.	SPECIFIC GRAVITY	VISCOSITY	TOTAL PROTEIN	ALBUMIN GLOBULIN	n	n_0	$p/RTCp$
47.....	1.0251	1.69	6.59	1.31	1.80	1.79	1.01
43.....	1.0255	1.62	6.59	1.43	1.74	1.80	0.96
21.....	1.0255	1.67	6.59	1.86	1.69	1.88	0.90
6.....	1.0277	1.72	6.59	1.86	1.61	1.88	0.85
28.....	1.0261	1.68	6.59	1.86	1.79	1.88	0.95
11.....	1.0264	1.73	6.59	1.86	1.88	1.88	1.00
80.....	1.0271	1.77	6.59	1.86	1.78	1.88	0.95
62.....	1.0271	1.73	6.59	2.03	1.56	1.91	0.94
25.....	1.0258	1.61	6.59	2.03	1.85	1.91	0.97
45.....	1.0262	1.67	6.59	2.24	1.85	1.94	0.95
91.....	1.0275	1.78	6.59	2.46	1.91	1.96	0.97
41.....	1.0260	1.68	6.59	2.46	1.96	1.96	1.00

$p/RTCp$ of 1.00 or higher (table 6), and here again we noticed the variation in the total protein from 6.04 to 7.47, in the A/G from 1.31 to 2.45, and in the value of n from 1.76 to 2.11. The value of 1.07 is not explained by us, except as an error in the determination of the total protein.

Pauli (11) discusses the relation between viscosity and colloid osmotic

TABLE 5

Group of cases with a value for $p/RTCp$ of less than 0.85

CASE NO.	SPECIFIC GRAVITY	VISCOSITY	TOTAL PROTEIN	ALBUMIN GLOBULIN	n	n_0	$p/RTCp$
1.....	1.0268	1.74	8.34	1.80	1.55	1.87	0.81
13.....	1.0270	1.72	7.69	1.17	1.41	1.73	0.81
16.....	1.0263	1.68	6.70	2.58	1.65	1.98	0.84
40.....	1.0287	1.85	7.91	2.29	1.57	1.94	0.81
66.....	1.0267	1.71	6.37	1.91	1.54	1.88	0.82
72.....	1.0248	1.65	6.05	2.71	1.80	1.99	0.81
77.....	1.0270	1.74	7.14	1.50	1.52	1.81	0.84
79.....	1.0271	1.78	7.14	1.91	1.52	1.89	0.80
84.....	1.0289	1.90	8.23	2.02	1.51	1.91	0.79
85.....	1.0325	2.32	9.11	0.78	1.33	1.60	0.83
88.....	1.0352	2.59	10.75	0.77	1.09	1.58	0.69
95.....	1.0272	1.82	6.92	1.00	1.23	1.68	0.74
98.....	1.0290	1.93	8.02	1.51	1.43	1.81	0.79
105.....	1.0298	1.96	7.47	2.81	1.67	2.00	0.83

TABLE 6

Group of cases showing values for $p/RTCp$ of 1.00 or over

CASE NO.	SPECIFIC GRAVITY	VISCOSITY	TOTAL PROTEIN	ALBUMIN GLOBULIN	n	n_0	$p/RTCp$
11.....	1.0264	1.73	6.59	1.86	1.88	1.88	1.00
19.....	1.0277	1.79	7.03	2.00	1.91	1.91	1.00
22.....	1.0275	1.72	7.47	1.16	1.72	1.73	1.00
26.....	1.0258	1.64	6.70	1.78	1.85	1.87	1.00
33.....	1.0263	1.71	6.37	2.26	1.94	1.94	1.00
38.....	1.0282	1.82	7.69	1.09	1.76	1.71	1.03
47.....	1.0251	1.69	6.59	1.31	1.80	1.79	1.01
55.....	1.0268	1.81	6.04	2.45	2.11	1.96	1.07
73.....	1.0261	1.68	6.37	2.06	1.92	1.91	1.00
59.....	1.0286	1.83	7.36	1.50	1.81	1.81	1.00

TABLE 7

Cases showing viscosity of 1.64 to 1.65

CASE NO.	SPECIFIC GRAVITY	VISCOSITY	TOTAL PROTEIN	ALBUMIN GLOBULIN	n_0	$p/RTCp$
4.....	1.0254	6.81	2.02	1.80	1.91	0.94
15.....	1.0257	7.02	2.02	1.72	1.89	0.89
17.....	1.0255	6.70	2.33	1.83	1.95	0.93
21.....	1.0255	6.59	1.86	1.69	1.88	0.90
26.....	1.0258	6.70	1.78	1.85	1.87	1.00
34.....	1.0247	6.59	1.71	1.80	1.85	0.97
35.....	1.0257	7.03	1.84	1.72	1.88	0.92
72.....	1.0248	6.05	2.71	1.80	1.99	0.81
102.....	1.0253	7.14	1.76	1.78	1.86	0.95

pressure in albumin solutions, showing the parallelism between them. In table 7 we selected a group of cases with a viscosity of 1.64 to 1.65. We noted that the protein concentration varied between 6.05 and 7.14, the A/G between 1.71 and 2.71, the value of n between 1.69 and 1.85, and the value of $p/RTCp$ between 0.81 and 1.00. If viscosity has any direct relation to colloid osmotic pressure we are not able to show it in our cases. It may well be that there are too many other factors which work in different directions to be able to show it here.

Finally we studied a group of cases with a specific gravity of 1.0272 to 1.0273 (table 8), and we noted that the protein concentration varied between 6.70 and 7.36, the A/G between 1.50 and 2.54, the value of n between 1.51 and 1.88, and the $p/RTCp$ between 0.79 and 0.97, showing that there is no general effect.

TABLE 8
Cases showing specific gravity of 1.0272 to 1.0273

CASE NO.	VISCOSITY	TOTAL PROTEIN	ALBUMIN GLOBULIN	n	n_0	$p/RTCp$
8.....	1.78	7.14	1.87	1.51	1.88	0.79
20.....	1.75	7.03	2.00	1.80	1.91	0.94
23.....	1.75	7.25	2.37	1.57	1.95	0.91
24.....	1.72	6.70	2.13	1.88	1.92	0.97
27.....	1.74	7.03	2.41	1.77	1.96	0.90
48.....	1.74	6.92	2.54	1.80	1.97	0.91
53.....	1.74	6.93	1.63	1.79	1.84	0.97
58.....	1.74	6.70	1.50	1.71	1.81	0.94
82.....	1.87	7.36	1.11	1.65	1.71	0.97

From these observations we can come to the general conclusion that the colloid osmotic pressure of human serum can not be predicted from a generalized formula, for there are too many factors which influence it besides the A/G , the protein concentration, the specific gravity or the viscosity. There is no doubt an intrinsic individuality in the physico-chemical conditions that are found in each serum, besides the many effects such as the electrolytic antagonism of ions, Na, K against Ca, Mg, as well as the cholesterol-phospholipin equilibrium which von Farkas (17) has shown affects the colloid osmotic pressure of sera. Fishberg (5) finds that the colloid osmotic pressure per gram of protein is higher in lipaemic bloods.

The comparison of the measured with the theoretical colloid osmotic pressure is an important criterion by which to judge the results obtained as well as the deviation from the expected value which pathological sera may have. It will also help to direct further research to elucidate other

factors that affect the measurement. We can at the same time mistrust obtained values which deviate very far from the theoretical expectation.

I wish to acknowledge to Prof. G. S. Adair the kindness and personal instruction as to the use of this method and to thank Dr. S. DeW. Ludlum for the interest and facilities given by him for the accomplishment of this work.

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X-RAY STUDIES ON THE HYDROUS OXIDES. IX

SCANDIUM OXIDE MONOHYDRATE¹

HARRY B. WEISER AND W. O. MILLIGAN

Department of Chemistry, The Rice Institute, Houston, Texas

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The addition of alkalis to solutions of scandium salts gives a white hydrous precipitate. Crookes (2) represented the composition of the air-dried gel by the formula $\text{Sc}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$, and Böhm and Niclassen (1) found that the gel gave an x-ray diffraction pattern different from that of the anhydrous oxide. More recently Štěrba-Böhm and Melichar (3) added freshly precipitated scandium oxide to boiling potassium hydroxide solutions and obtained from this mixture definite crystals which, after washing with alcohol, had a composition represented by the formula $\text{K}_2[\text{Sc}(\text{OH})_5 \cdot \text{H}_2\text{O}] \cdot 3\text{H}_2\text{O}$. This compound was hydrolyzed on washing with water, giving a product which was formulated as $[\text{2Sc}(\text{OH})_3] \cdot \text{H}_2\text{O}$ ($= \text{Sc}_2\text{O}_3 \cdot 4\text{H}_2\text{O}$).

The preparations analyzed by Crookes and by Štěrba-Böhm and Melichar were not dried under equilibrium conditions, and therefore their analysis of the products is insufficient to establish the existence of the alleged hydrates of hydrous scandium oxide. The x-ray data of Böhm and Niclassen indicate that the precipitated oxide is either some definite hydrate or a second modification of the oxide. This paper gives the isobaric dehydration and x-ray diffraction analysis of four samples of precipitated scandia.

EXPERIMENTAL

Preparation of samples

Sample A. To 100 cc. of a 0.1 *M* solution of scandium chloride at 25°C. was added a slight excess of ammonium hydroxide solution. The resulting white gelatinous precipitate was similar to hydrous alumina prepared in the same manner.

Sample B was prepared like sample A except that the scandium chloride solution was at 100°C. This precipitate was somewhat less gelatinous in appearance and settled more rapidly than sample A.

¹ A preliminary report was presented at the Ninety-first Meeting of the American Chemical Society, held in Kansas City, Missouri, April, 1936.

Sample C was prepared in the same manner as sample A, but from a different supply of scandium chloride.

Sample D. Scandium oxide gel precipitated at 25°C. (*cf.* sample A) was washed rapidly, using the centrifuge, and added at once to a boiling solution of potassium hydroxide. Part of the gel dissolved and part was peptized,

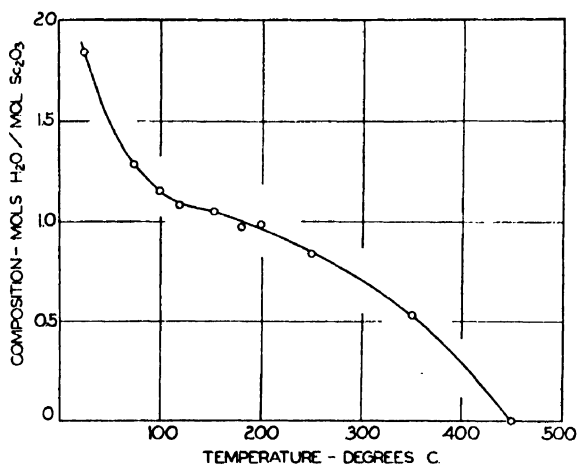


FIG. 1. Dehydration isobar for hydrous $\text{Sc}_2\text{O}_3 \cdot \text{H}_2\text{O}$ (sample A)

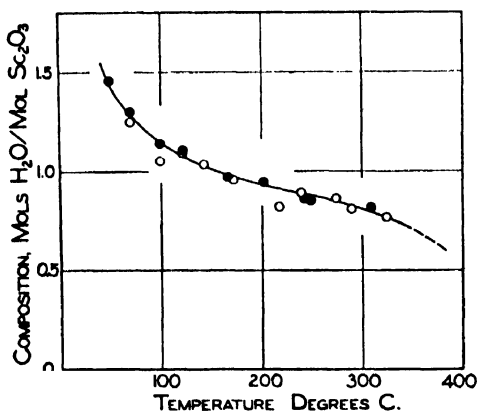


FIG. 2

FIG. 2. Dehydration isobar for hydrous $\text{Sc}_2\text{O}_3 \cdot \text{H}_2\text{O}$ (sample B)

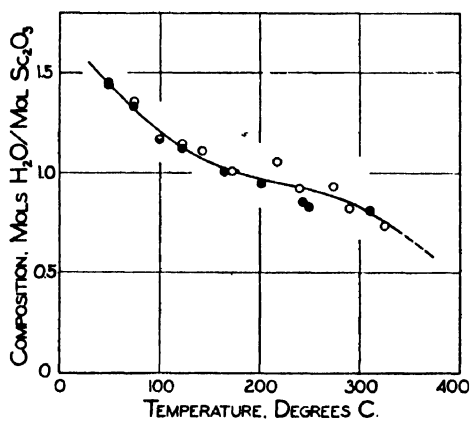


FIG. 3

FIG. 3. Dehydration isobar for hydrous $\text{Sc}_2\text{O}_3 \cdot \text{H}_2\text{O}$ (sample C)

giving a cloudy sol. After centrifuging the mixture at 2500 R.P.M. for 5 minutes to remove suspended material, it was allowed to stand 2 days until a considerable amount of a powdery precipitate had formed on the bottom and sides of the flask.

Each of the above four samples was washed with 50-cc. portions of water by the aid of a centrifuge until the wash water gave no test for chloride

(hydroxide in the case of sample D), after which they were air-dried at room temperature.

Dehydration isobars

Samples A, B, and C were dehydrated in an apparatus already described (4, 6) at an aqueous vapor pressure of 23.6 mm. The resulting isobars are given in figures 1 to 3. It is obvious from these curves that

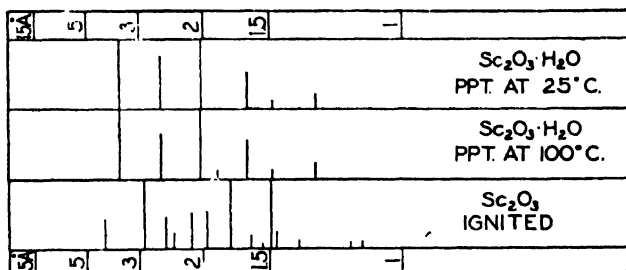


FIG. 4. X-ray diffraction patterns

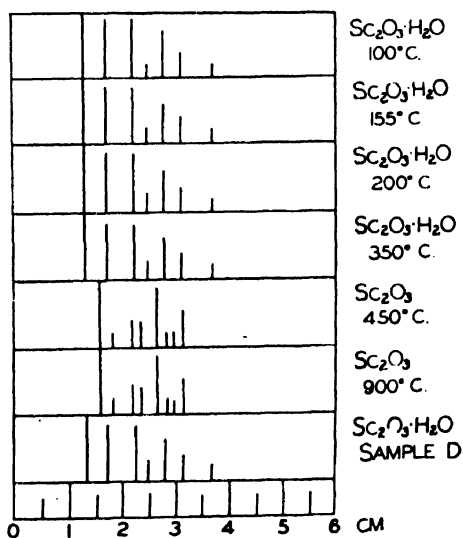


FIG. 5. X-ray diffraction patterns

scandia precipitated at 25°C. and at 100°C. is the monohydrate $\text{Sc}_2\text{O}_3 \cdot \text{H}_2\text{O}$, corresponding to precipitated alumina, which is $\gamma\text{-Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$.

X-ray examination

X-ray diffraction patterns were obtained for samples A and B with the General Electric apparatus. The samples in "nonex" glass tubes were examined with Mo K_α x-radiation; the exposure time was about 30 hours.

The films were standardized against pure sodium chloride in the usual way. The positions and intensities of the diffraction lines are represented in chart form in figure 4. The close resemblance between the diffraction patterns of $\text{Sc}_2\text{O}_3 \cdot \text{H}_2\text{O}$ and the corresponding $\gamma\text{-Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$ (5) indicates a similarity in crystal structure.

Portions of sample C which had been dehydrated at temperatures of 100°, 155°, 200°, 350°, 450°, and 900°C., and of sample D were examined using Cu K_α x-radiation; the camera diameter was 57.6 mm. and the exposure time 30 to 60 minutes. To prevent gain or loss of water during examination, the samples were sealed in tubes of Lindemann glass following the procedure previously described (4, 6). The several patterns are represented diagrammatically in figure 5. They show (a) that the monohydrate lattice persists until the samples are almost anhydrous and (b) that but one modification of the anhydrous oxide exists between 450° and 900°C.

Sample D, prepared by a procedure similar to that of Štěrba-Böhm and Melichar, gave the same x-ray diffraction as the precipitated gel, $\text{Sc}_2\text{O}_3 \cdot \text{H}_2\text{O}$. It is probable, therefore, that the alleged compound, $[\text{2Sc}(\text{OH})_3] \cdot \text{H}_2\text{O}$ or $\text{Sc}_2\text{O}_3 \cdot 4\text{H}_2\text{O}$, of Štěrba-Böhm and Melichar is hydrous $\text{Sc}_2\text{O}_3 \cdot \text{H}_2\text{O}$.

SUMMARY

The following is a brief summary of the results of this investigation:

1. The addition of alkalis to solutions of scandium salts at 25°C. or 100°C. throws down a white, highly hydrous precipitate.
2. Isobaric dehydration studies show that the precipitated gel is hydrous $\text{Sc}_2\text{O}_3 \cdot \text{H}_2\text{O}$.
3. X-ray diffraction examination shows scandium oxide monohydrate to have a crystalline structure distinct from that of the anhydrous oxide, but similar to that of $\gamma\text{-Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$.
4. There is no indication of a second modification of anhydrous Sc_2O_3 between temperatures of 450°C. and 900°C.
5. The alleged compound $[\text{2Sc}(\text{OH})_3] \cdot \text{H}_2\text{O}$ of Štěrba-Böhm and Melichar is probably hydrous $\text{Sc}_2\text{O}_3 \cdot \text{H}_2\text{O}$.

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THE HYDROUS OXIDES OF SOME RARER ELEMENTS¹

HARRY B. WEISER AND W. O. MILLIGAN

Department of Chemistry, The Rice Institute, Houston, Texas

March 21, 1938

The composition of the precipitated oxides of aluminum (5, 10), gallium (8), indium (8), thallium (8), and scandium (14) has been established as a result of x-ray diffraction and isobaric dehydration studies on the several compounds. This paper is concerned with the application of similar methods of investigation to the remaining oxides of Group III, about which little authentic information was available. For the purpose of this summarizing report, the oxides of the metals under consideration will be classified into (a) the aluminum family (gallium, indium, thallium), (b) the scandium family (scandium, yttrium), and (c) the rare earths (neodymium, praseodymium, samarium).

EXPERIMENTAL

Following procedures already described (11, 12, 13, 15), dehydration isobars of the several preparations were obtained, taking care to allow sufficient time (days or weeks) for equilibrium to be established at each temperature point on the isobar.

Samples for x-ray diffraction analysis were taken at various temperatures from separate portions which had been heated in the same way and at the same time as the weighed samples for dehydration isobars. After sealing (9, 13, 15) in thin tubes of Lindemann glass, the samples were exposed to filtered Cu K α x-radiation in a camera 57.6 mm. in diameter.

THE ALUMINUM FAMILY

Previous investigations (8) have shown that precipitated gallium oxide consists of hydrous particles of α -Ga₂O₃ when precipitated rapidly and unaged. The oxide prepared by slow precipitation from ammonium hydroxide solution or after aging may consist of hydrous Ga₂O₃·H₂O. Precipitated indium oxide is hydrous In₂O₃·3H₂O or In(OH)₃. Hydrous thallic oxide prepared by precipitation (6) or by Carnegie's (2) method (which was said to give a definite trihydrate) shows no indication of

¹ Presented at the Second Annual Symposium of the Division of Physical and Inorganic Chemistry,—A Symposium on the Less Familiar Elements,—held at Cleveland, Ohio, December 27-29, 1937.

hydrate formation. Dehydration isobars for the various samples are collected in figure 1. The isobar for hydrous thallic oxide is taken from the work of Hüttig and Mytyzek (6). X-ray diffraction patterns showing the chemical individuality of the several hydrous oxides and hydrates are given in figures 4, 5, and 6, respectively.

THE SCANDIUM FAMILY

In the preceding paper (14) it was shown that precipitated scandia is the monohydrate $\text{Sc}_2\text{O}_3 \cdot \text{H}_2\text{O}$, corresponding to precipitated alumina, which is $\gamma\text{-Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$. In figure 4 is given a diagram of the x-ray diffraction patterns of $\text{Ga}_2\text{O}_3 \cdot \text{H}_2\text{O}$, $\text{Sc}_2\text{O}_3 \cdot \text{H}_2\text{O}$, and $\gamma\text{-Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$. It will be noted that

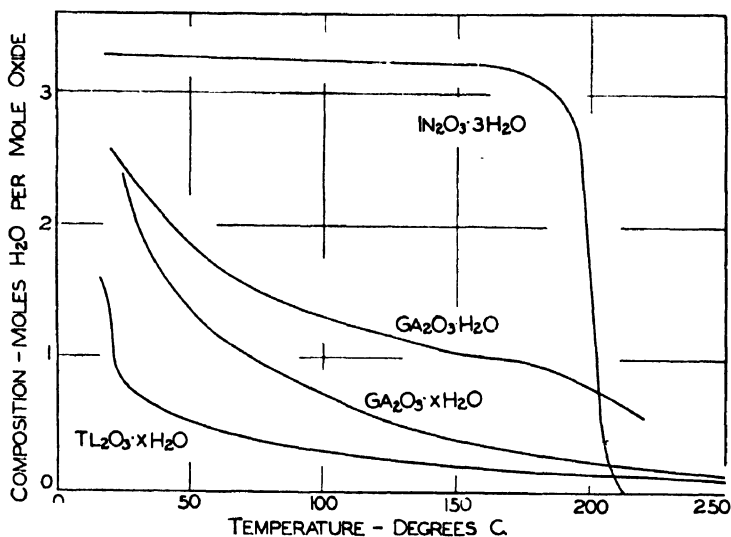


FIG. 1. Dehydration isobars for the hydrous oxides and hydrates of gallium, indium, and thallium.

the patterns of the alumina and scandia monohydrates are very similar except for a uniform displacement of the lines. This furnishes additional evidence in support of the chemical individuality of $\gamma\text{-Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$, even though the dehydration isobar for precipitated alumina is not a step curve (5, 12) corresponding to a monohydrate like that of $\text{Sc}_2\text{O}_3 \cdot \text{H}_2\text{O}$ (figure 2).

No evidence is available concerning the constitution of precipitated yttria, except the observation of Böhm and Niclassen (1) that the freshly precipitated gel is amorphous to x-rays, becoming microcrystalline after prolonged aging. A sample of yttria was prepared by the interaction of solutions of yttrium chloride and ammonium hydroxide at 25°C ., followed by washing with the aid of a centrifuge and air drying. The isobar for

this preparation is a continuous curve (figure 2) with no indication of hydrate formation. In agreement with the results of Böhm and Niclasen, the x-ray diffraction pattern of the freshly formed product consists of two broad diffuse bands (figure 6). Aging experiments have not yet been carried out.

THE RARE EARTHS

Damiens (4) claimed that the composition of the precipitated oxides of neodymium, praseodymium, and samarium was represented by the respective formulas $\text{Nd}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$, $\text{Pr}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$, and $\text{Sm}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$. Joye and Garnier (7) found that precipitated neodymium oxide retained 3.0, 1.5, and 1.0 moles of water per mole of oxide when the samples were dried

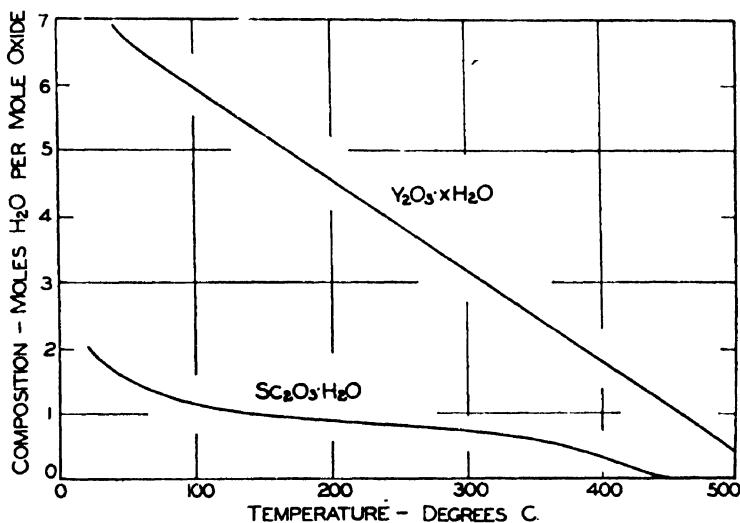


FIG. 2. Dehydration isobars for hydrous scandium oxide monohydrate and yttrium oxide.

at room temperature, 320°C., and 520°C., respectively. The evidence of Damiens and of Joye and Garnier is not conclusive, since (a) it is not known whether the analyzed products were in equilibrium with a fixed pressure of aqueous vapor at the temperature of drying, and (b) there are not enough data to establish an isobar.

In this investigation samples of precipitated neodymium, praseodymium, and samarium oxides were prepared as described above for yttrium oxide. The dehydration isobars for samples precipitated at 100°C. are given in figure 3. It is apparent that precipitated neodymium and praseodymium oxides consist of the hydrous trihydrate or hydroxide. There is only the slightest indication of a break in the samarium oxide isobar at the composition corresponding to the trihydrate. The neodymium isobar shows some

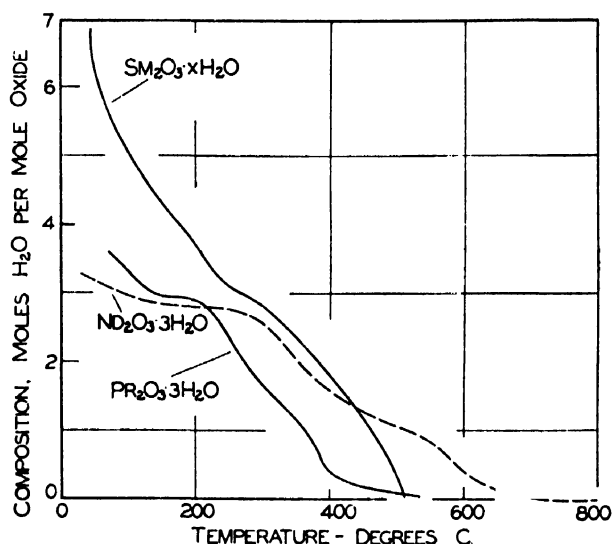


FIG. 3. Dehydration isobars for the hydrous oxides and hydrates of neodymium, praseodymium, and samarium.

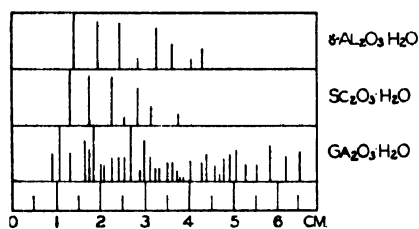


FIG. 4

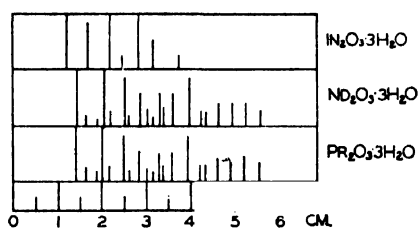


FIG. 5

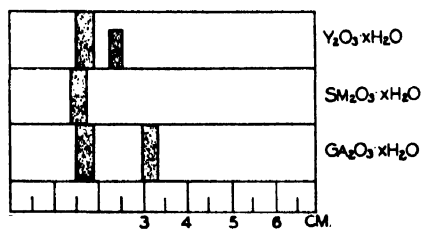


FIG. 6

FIG. 4. X-ray diffraction patterns for the trihydrates of the oxides of indium, neodymium, and praseodymium.

FIG. 5. X-ray diffraction patterns for the hydrous monohydrates of the oxides of aluminum, scandium, and gallium.

FIG. 6. X-ray diffraction patterns for the hydrous oxides of yttrium, samarium, and gallium.

indication and the praseodymium isobar a slight indication of the formation of monohydrate at temperatures around 400°C.

X-ray diffraction patterns of $\text{Nd}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ are given in figure 5. These patterns are distinct from the patterns of the respective anhydrous oxides. There is some indication of a new crystalline phase in the x-radiograms of samples of neodymium oxide dehydrated at temperatures around 400° to 500°C. These new diffraction lines are distinct from the lines of the trihydrate or anhydrous oxide. This evidence supports the suggestion that a monohydrate of neodymium oxide may exist.

The x-ray diffraction pattern of precipitated samarium oxide consists of one, or possibly two, very broad, diffuse bands. In the absence of a definite break in the dehydration isobar and a well-defined x-radiogram, the present authors prefer to consider this material to be hydrous samarium oxide, and not a definite hydrate or hydroxide.

SUMMARY

The following is a brief summary of the results of this paper:

1. But few early studies have been made of the hydrous oxides and hydrous hydrates of the Group III metals other than aluminum. In this report the composition of the hydrous oxides and hydrous hydrates of gallium, indium, thallium, scandium, yttrium, neodymium, praseodymium, and samarium have been investigated from the standpoint of their dehydration isobars and x-ray diffraction patterns.

2. The dehydration isobars have been obtained under conditions that ensure the establishment of equilibrium at each point of the isobar.

3. Samples for x-ray diffraction examination were removed and sealed in thin tubes of Lindemann glass under conditions that ensure neither loss nor gain of water vapor.

4. The precipitated oxides of indium, neodymium, and praseodymium consist of the hydrous trihydrates or hydroxides.

5. The precipitated oxides of gallium (when formed slowly or aged) and of scandium are hydrous monohydrates.

6. The precipitated oxides of thallium, gallium (when formed rapidly or unaged), yttrium, and samarium show no indication of hydrate formation. These precipitated gels should be considered as hydrous oxides of the respective metals.

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THE SORPTION OF CHLORINE BY ACTIVATED CHARCOAL¹

L. H. REYERSON AND A. W. WISHART

School of Chemistry, University of Minnesota, Minneapolis, Minnesota

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In a previous communication (5) the authors described a method for determining the sorption of chlorine by porous sorbents, which was a modification of the method given earlier by Cameron and Reyerson (1), and presented the results of a series of measurements on the sorption of chlorine by silica gel. The results of a similar series of measurements on the sorption of chlorine by activated charcoal are given at this time. The charcoal used in this study was a part of the material prepared by Cameron for use in the work reported by Reyerson and Cameron (3, 4). It was steam-activated at 850°C. and allowed to cool to room temperature before air was admitted. The steam-activated charcoal was then placed in a silica bulb and heated to 700°C. under high vacuum for 24 hours. Upon cooling to room temperature, oxygen was admitted. After standing several hours in oxygen the charcoal was heated once more, pumped out for 48 hours, and finally cooled in an atmosphere of nitrogen. Weighed amounts of this charcoal were placed in the glass bucket of the McBain-Bakr balance. The quantities of chlorine sorbed by this charcoal were determined at 35.5°, 51°, 73.5°, and 91.5°C. over a pressure ranging from zero to about atmospheric pressure. The chlorine was purified, introduced into the system, and maintained at the various vapor pressures as previously described (5). The results are given in table 1 and presented graphically in figure 1. As shown in figure 1 a slight hysteresis exists in the desorption points near 100 mm. pressure. Slightly more chlorine was retained during desorption than was taken up during adsorption. Since the establishment of equilibrium was slow, as shown in table 1, it may well be that the observed differences were due to the fact that equilibrium was not quite attained. However, similar results were observed in the sorption of bromine by the same activated charcoal (3).

It was found impossible to remove all of the sorbed chlorine under prolonged evacuation at elevated temperatures. The final desorption points reached by two methods of drastic treatment are shown in the figure.

¹ The material here presented formed a part of a thesis submitted to the Graduate Faculty of the University of Minnesota by Arthur W. Wishart in partial fulfillment of the requirements for the degree of Doctor of Philosophy, August, 1937.

Curves of the type here obtained are typical of a Langmuir type of sorption. This was further borne out by plotting values against the X/M $P/(X/M)$. A straight line is demanded by the Langmuir theory, and this was found when the values in table 2 were plotted as shown in figure 2. It

TABLE 1
Sorption of chlorine by activated charcoal

PRESSURE (COR- RECTED)	GAS (CHLO- RINE) SORBED PER GRAM OF CHARCOAL	X/M PER GRAM OF SORBENT	TIME FOR READING	PRESSURE (CORRECTED)	GAS (CHLO- RINE) SORBED PER GRAM OF CHARCOAL	X/M PER GRAM OF SORBENT	TIME FOR READING
Isothermal at 35.5°C.				Isothermal at 73.5°C.			
mm.		millimoles	hours	mm.		millimoles	hours
0.0*	0.0	0.0		0.0*	0.0	0.0	
81.6	0.3559	5.0192	24	25.2	0.2750	3.8781	20
227.3	0.3799	5.3579	18	260.2	0.3438	4.8481	20
348.7	0.3869	5.4552	15	586.5	0.3634	5.1245	18
526.0	0.3962	5.5873	12	720.3	0.3738	5.2714	12
672.3	0.3997	5.6360	12	610.5	0.3645†	5.1406†	12
409.1	0.3938†	5.5526†	15	303.0	0.3504†	4.9411†	14
103.6	0.3688†	5.2000†	15	127.1	0.3305†	4.6612†	18
24.0	0.3433†	4.8405†	18	24.2	0.2869†	4.0454†	20
6.9	0.3092†	4.3600†	24	18.2	0.2730†	3.8495†	20
0.00†	0.2327†	3.2815†	48				
Isothermal at 51.0°C.				Isothermal at 91.5°C.			
mm.		millimoles	hours	mm.		millimoles	hours
0.0*	0.0	0.0		0.0*	0.0	0.0	
15.3	0.2903	4.0935	24	25.7	0.2663	3.7552	20
136.7	0.3503	4.9399	20	142.5	0.3101	4.3731	18
324.3	0.3703	5.2220	16	248.0	0.3294	4.6455	15
474.8	0.3775	5.3229	16	566.3	0.3543	4.9966	15
682.0	0.3892	5.4888	12	721.8	0.3587	5.0584	12
399.9	0.3735†	5.2673†	16	591.3	0.3554†	5.0113†	16
67.1	0.3404†	4.8006†	20	330.4	0.3426†	4.8300†	18
6.8	0.2853†	4.0238†	24	138.9	0.3211†	4.5282†	18
				31.9	0.2813†	3.9672†	20
				10.5	0.2432†	3.4294†	20
				0.00†	0.1799†	2.5369†	36

* Readings in rows indicated in this manner were taken with the system evacuated and before admission of the halogen.

† Chlorine frozen down by liquid oxygen.

‡ Desorption readings.

appeared from these results that we were dealing with a monomolecular type of sorption. Since equilibria were established slowly, it seemed likely that the sorptions were of an activated type. Calculations of differential heats of sorption tended to confirm this idea. An average of nine of these values gave 8860 calories per mole as the differential heat of sorp-

tion. This is significantly larger than the heat of vaporization at the boiling point, 4778 calories, and indicates strong forces of attraction between the chlorine atoms and sorption centers on the carbon surface.

The type of sorption curve for chlorine on charcoal is fundamentally different from that of chlorine on silica gel (1), but it is almost exactly like that of bromine on activated charcoal (3). Furthermore, the quantity in millimoles of chlorine sorbed at a given temperature is about the same as the amount of bromine taken up at a like temperature above its boiling point. In figure 3 the isotherms of the sorption of chlorine, bromine, and iodine by charcoal are given. A similar comparison for the sorption of

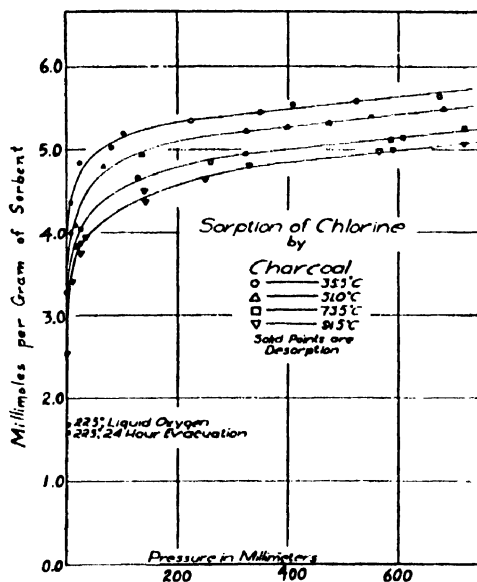


FIG. 1. Sorption of chlorine by steam-activated charcoal at different temperatures and pressures

these halogens by silica gel is shown in figure 4. These two figures show the differences in the type of sorption exhibited by charcoal and silica gel for the halogens. Figure 3 shows that the sorptive capacity of charcoal for bromine and chlorine is about the same, while it is more than tenfold greater than for iodine. Since the sorptions of all of these halogens fit the Langmuir expression for a monomolecular layer of sorbed molecules, it may well be that the iodine molecules are enough larger than the bromine molecules so that steric hindrance prevents the iodine molecules from being sorbed on most of the active centers of the carbon surface. Weaker forces existing between the carbon and the iodine may account for some of the difference, but it does not seem probable that a shorter average life of

TABLE 2
Sorption values used in Langmuir equation

P Pressure	X/M PER GRAM OF CHARCOAL	$\frac{P}{X/M}$	P PRESSURE	X/M PER GRAM OF CHARCOAL	$\frac{P}{X/M}$
Isothermal at 35.5°C.			Isothermal at 73.5°C.		
mm.	millimoles		mm.	millimoles	
6.9	4.3600	1.582	18.2	3.8495	4.728
24.0	4.8405	4.958	24.2	4.0454	5.982
81.6	5.0192	16.257	25.2	3.8781	6.498
103.6	5.2000	19.923	127.1	4.6612	27.268
227.3	5.3579	42.423	260.3	4.8481	53.691
348.7	5.4552	63.920	303.0	4.9411	61.322
409.1	5.5526	73.677	586.5	5.1245	114.450
526.0	5.5826	94.221	610.5	5.1406	118.760
672.3	5.6360	119.286	720.3	5.2714	136.643
Isothermal at 51.0°C.			Isothermal at 91.5°C.		
6.8	4.0238	1.600	10.5	3.4294	3.062
15.3	4.0935	3.738	25.7	3.7552	6.844
67.1	4.8006	13.977	31.9	3.9672	8.041
136.7	4.9399	27.672	138.9	4.5282	30.674
324.3	5.2220	62.103	142.5	4.3731	32.585
399.9	5.2673	75.921	248.0	4.6455	53.385
474.8	5.3229	89.199	330.4	4.8309	68.393
682.0	5.4885	124.253	566.3	4.9966	113.337
			591.3	5.0113	117.993
			721.8	5.0584	142.693

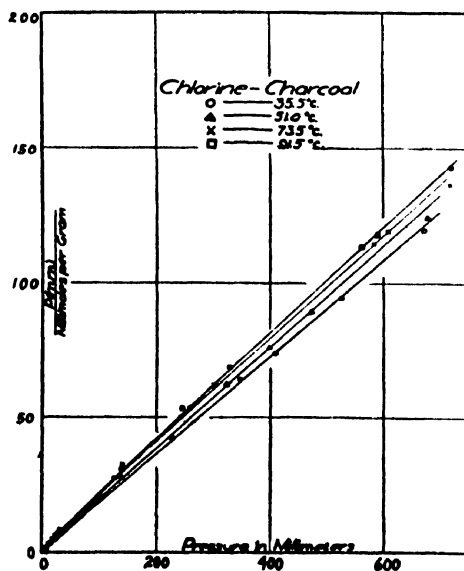


FIG. 2. Sorption isotherms obtained by use of the Langmuir equation

iodine on the carbon surface could be responsible for the tenfold decrease in sorption.

If steric hindrance prevents many of the active centers from taking up iodine but not chlorine or bromine, then it should be possible to obtain some idea concerning the spacing of active centers on activated charcoal. From viscosity measurements the radii of the halogen molecules are given as follows: chlorine, 1.85 Å.; bromine, 2.02 Å.; and iodine, 2.23 Å. Recent x-ray studies on solid bromine (6) and solid iodine (2) give the following distances between the halogen atoms of the molecules in the crystal lattice: Br—Br = 2.27 Å. and I—I = 2.70 Å. However, the absence of a like value for chlorine led us to use the values from viscosity data for compari-

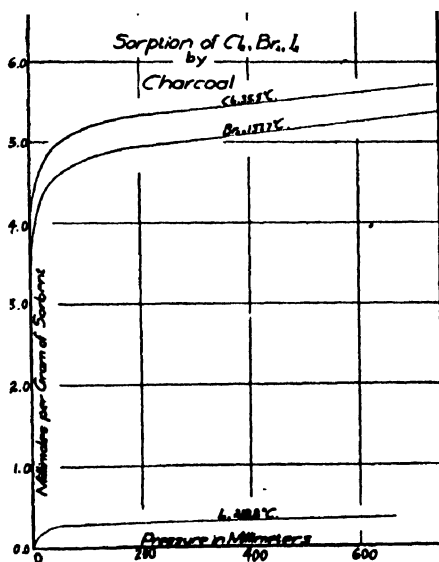


FIG. 3. Sorption of chlorine, bromine, and iodine by charcoal

son. If, for convenience, we assume the cross sections of the molecules to be circles, then the area covered will be 1.07×10^{-15} cm.² by a chlorine molecule, 1.28×10^{-15} cm.² by a bromine molecule, and 1.56×10^{-15} cm.² by an iodine molecule. If the effective area is the same as this cross section, then the critical area from the steric hindrance point of view must lie between 1.28 and 1.56×10^{-15} cm.² The real areas occupied by these molecules are probably somewhat greater than this, in view of the results of the x-ray studies and the knowledge of the probable shape of the molecules. Even so, the minimum spacing of the active centers on the charcoal surface must be somewhere between 2.5 Å and 3.2 Å. If the chlorine and bromine molecules occupy all of the active centers in a checkerboard arrangement, then the minimum area of charcoal covered by chlorine

molecules comes out to be $4.31 \times 10^6 \text{ cm.}^2$ per gram of charcoal. A similar calculation for bromine gives a minimum area of $5.54 \times 10^6 \text{ cm.}^2$ per gram. It is more than likely that the surface area of the charcoal used in these investigations is somewhat larger than these values. It is also possible that each atom of the halogen molecule is held by the carbon surface. If so, the spacing of the active centers may be such that they are able to hold the chlorine and bromine atoms without too much strain but not the iodine atoms.

These studies prove the very great difference that exists between the character of sorption on silica gel and charcoal. The surfaces of these two sorbents are of about the same magnitude, yet the whole character of the sorption is different. It should also be noted that the three halogens differ among themselves in the manner in which they are sorbed by silica

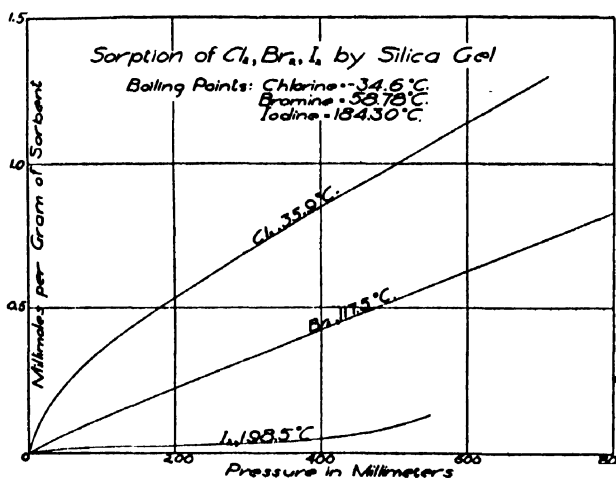


FIG. 4. Sorption of chlorine, bromine, and iodine by silica gel

gel. Further work will be needed to explain these differences. It is also suggested that the temperature of the sorbent surface plays a distinct rôle in the sorption process. The energy of the surface may be such that the amount of sorption is greatly reduced in spite of the fact that the sorbate at the temperature studied is below the critical temperature or even near the boiling point. Further study is in progress in the hope that additional light may be thrown on the problem.

SUMMARY

1. Sorption isotherms for chlorine on activated charcoal were obtained at 35.5° , 51.0° , 73.5° , and 91.5°C .
2. Comparison of these results with those of bromine and iodine is made.

3. Calculations show the minimum surface area of the activated charcoal to be 5.54×10^6 cm².

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HELMHOLTZ AND NERNST

WILDER D. BANCROFT

Cornell University, Ithaca, New York

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About sixty years ago Helmholtz (4) worked out an equation for the electromotive forces of concentration cells with diffusion. For a cell of the type



Helmholtz wrote an equation which is equivalent to:

$$E = RT \frac{u}{u+v} \int_{h_2}^{h_1} h \frac{\partial \ln p}{\partial h} dh \quad (1)$$

Here h is the dilution, or grams of water per gram of salt, instead of the concentration, which is the term we usually use nowadays. Helmholtz wrote $1 - n$, but I have changed that to conform with the modern custom. This equation can be right only when the transference number for the anion is independent of the concentration or dilution. This is usually not the case, and Helmholtz (3) discusses the matter very briefly in a later paper. The assumption is made throughout that water vapor follows the simple gas law $PV = RT$.

A few years later Helmholtz (5) discussed the case of concentration cells without diffusion. As typical he took reversed calomel cells



The formula, as written by Helmholtz, is equivalent to:

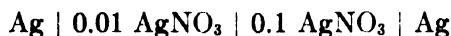
$$E = RT \int_{h_2}^{h_1} h \frac{\partial \ln p}{\partial h} dh \quad (2)$$

From Moser's data on the vapor pressures of zinc chloride solutions, Helmholtz calculated two interpolation formulas, which differ only slightly and which he called "a" and "b". For cells in which the two values of h are 0.8 and 9.1992 the observed and calculated values at temperatures varying between 17.7°C. and 21°C. were as given in table 1.

Helmholtz considered that his standard calomel cell had an electromotive force of about 1.043 volts, but he felt that the determinations of the

ohm were so uncertain at that time that it was safer to give his observations in terms of his standard calomel cell. That means that the values in table 1 should be increased by approximately 4 per cent to give them in what he considered to be millivolts. The important thing is that he was able to calculate the electromotive force with surprising accuracy even though one of his solutions contained less than 1 gram of water per gram of zinc chloride.

In 1889 Nernst (6) applied the van't Hoff theory of osmotic pressure and the Arrhenius theory of electrolytic dissociation to the case of concentration cells. For a cell of the type



Nernst deduces the equation:

$$E = 0.860T \frac{2v}{u+v} \ln \frac{P_2}{P_1} \times 10^{-4} \text{ volt} \quad (3)$$

where P_1 and P_2 are the osmotic pressures of the silver ions in the two solutions, respectively. Complete dissociation is assumed, and it is postulated

TABLE 1
Electromotive force in terms of calomel cell

Observed	Maximum	0.11648
	Minimum	0.11428
Mean for 13 days		0.11541
Calculated	(a)	0.11579
	(b)	0.11455

tacitly that the transference number for the anion does not change with the concentration. On the same postulation with regard to change of transference number with dilution, Helmholtz (2) derived an approximately correct expression for the electromotive force which is essentially identical with the Nernst equation, since in it the electromotive force is proportional to the logarithm of the concentrations of the salt in the two solutions.

Nernst (reference 5, p. 163) rewrote the Helmholtz formula for a silver nitrate concentration cell with diffusion, making it read:

$$E = \frac{\pi_0 - \pi}{\pi_0} \cdot \frac{MS}{\text{H}_2\text{O}} \cdot 0.000933 \pi_0 V_0 \frac{v}{u+v} \ln \frac{C_2}{C_1} \times 10^{-8} \text{ volt} \quad (4)$$

π_0 is the vapor pressure of liquid water at the temperature of the experiment; π that of a solution containing S grams of water per gram of salt; V_0 the volume of 1 gram of water vapor at the temperature in question and the pressure π_0 ; 0.000933 the amount of water in grams decomposed by

the electromagnetic unit of the quantity of electricity; and M/H_2O , finally, the amount of the salt decomposed by a quantity of electricity which decomposes 18 g. of water. When we compare this equation with equation 3 we see that at high dilutions osmotic pressure, P , and concentration, c (weight of salt per weight of water), are proportional one to the other, and consequently

$$\ln \frac{P_2}{P_1} = \ln \frac{c_2}{c_1}$$

If we are applying equation 4 to an electrolyte composed of univalent radicals, then $M = 2m$, where m is the molecular weight of the latter. The factor $2 \times 0.000933 \times \pi_0 V_0$ works out, in conjunction with Regnault's data, to 0.02542×10^{-8} in absolute c.g.s. units at 20°C . If we notice that V_0 is proportional to the absolute temperature and introduce this into equation 4, we get:

$$E = \frac{\pi_0 - \pi}{\pi_0} \cdot \frac{MS}{18} \cdot 0.867 T \frac{u}{u + v} \ln \frac{P_2}{P_1} \times 10^{-4} \text{ volt} \quad (5)$$

For equation 3 and equation 5 to be compatible, we must have

$$\frac{\pi_0 - \pi}{\pi_0} \cdot \frac{MS}{18} = 2 \quad (6)$$

The constants of the two formulas, 0.860 and 0.867, would be equal if water vapor at this temperature, as assumed by Helmholtz, and hydrogen ion, as assumed by Nernst, really behaved like ideal gases.

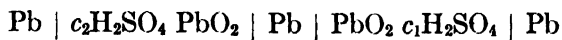
If we replace $MS/18$ by ν_2/ν_1 , where $\nu_2 = S/18$, the number of molecules of the solvent (water), and $\nu_1 = 1/m$, the corresponding value for the solute, we then have

$$(\pi_0 - \pi)/\pi_0 = 2\nu_1/\nu_2$$

The factor 2 arises from the fact that each molecule of a uni-univalent electrolyte gives two ions.

This is a case where the hand is quicker than the eye. In the Helmholtz equation we had the change of the partial pressure with the change of dilution. That does not integrate to $\ln \frac{P_2}{P_1}$ or $\ln \frac{c_2}{c_1}$ unless the dissolved substance behaves like an ideal gas of constant molecular weight. There cannot be any change of dissociation or any heat of dilution. Since the undissociated salt, if any, affects the vapor pressure, the Helmholtz and the Nernst formulas are identical only for infinitely dilute solutions. Since the Helmholtz equation is applicable at all concentrations, the Nernst equation must be in error to some extent at all finite concentrations.

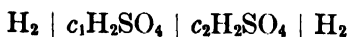
Dolezalek (1) has applied a simplified form of Helmholtz's equation to reversed lead storage cells,



For a change from 50.73 per cent to 35.82 per cent sulfuric acid the E.M.F. was 0.13 volt (calculated) and 0.13 volt (observed). For a change from 35.82 per cent to 19.07 per cent sulfuric acid the calculated value was 0.12 volt and the observed value 0.11 volt. When larger jumps were made, the results were poorer. Dolezalek made no attempt to apply exact theory and was rather pleased with the results he obtained.

Since the vapor pressures of sulfuric acid are thoroughly abnormal, owing to the high heat of dilution, and since nobody will claim 100 per cent dissociation for 50 per cent sulfuric acid, let alone 70 per cent acid, it is evident that the ion concentration is not the sole factor in determining the electromotive force. The lead storage cell should be studied with care over as wide a range of concentrations as possible and then compared with the most accurate formula obtainable.

One can also do a hydrogen-lead peroxide cell up to the concentration at which the solubility of lead sulfate becomes a serious factor. If a satisfactory equation can be developed for the change of the transference number with the concentration it would be possible to study the cell

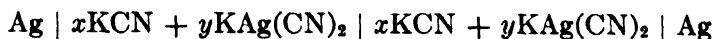


up to the concentration at which the hydrogen reduces sulfuric acid.

If the transference problem can be solved, hydrogen electrodes with hydrochloric acid and with acetic acid will show the applicability of the Helmholtz equation to strong acids and weak acids. Since the undissociated part of an acid affects the electromotive force of a hydrogen concentration cell, and since the nature of the anion affects the dissociation, the nature of the anion will affect the apparent concentration quite apart from any effect due to the displacement of the water equilibrium.

One would also like to see experiments with cadmium and cadmium iodide concentration cells in methyl alcohol where the transference number is negative over quite a range of concentrations. Cadmium and cadmium chloride in water will give an extreme case of abnormally small dissociations. All cases of this type can be calculated by means of the Helmholtz formula once one has the data. There are some cases, however, to which the Helmholtz formula is certainly not applicable at present and perhaps may never be.

If we take a cell,



and add a little silver cyanide to one solution, there should be practically

no change in partial pressure because one is merely replacing a cyanide ion by a silver cyanide ion. Consequently no accurate equation for this type of cell can be formulated in the present state of our knowledge.

The general results of this paper are as follows:

1. The Helmholtz equations for concentration cells coincide with the corresponding equations deduced by Nernst only at infinite dilution.
2. Since the Helmholtz equations are sound thermodynamically, it follows that the Nernst equations are accurate only at infinite dilution. It is not surprising, therefore, that one cannot run up even to moderate concentrations.
3. Since the Helmholtz equations involve the change of the vapor pressure with the concentration, the electromotive force depends also on the concentrations of the undissociated salt, base, or acid.
4. Dolezalek's rather crude application of the Helmholtz theory to the lead storage cell gives pretty good results for the change of electromotive force with change of sulfuric acid concentration. If the work were done well, the agreement would undoubtedly be excellent.
5. For reversed zinc-calomel concentration cells Helmholtz was able to get results to within 1 millivolt, even with a solution containing more than 1 gram of zinc chloride per gram of water.
6. It should be possible to calculate accurately the electromotive forces of hydrogen-sulfuric acid cells with diffusion up to concentrations at which hydrogen reduces sulfuric acid in a reasonable period of time.
7. Apparently no determination of pH in biological systems can be considered even approximately accurate, though we do not yet know the magnitude of the error.
8. At present nobody knows how to handle adequately the problem of electromotive forces in systems involving complex salts.

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NEW BOOKS

The Newer Alchemy. By LORD RUTHERFORD. 67 pp. London: Cambridge University Press, 1937. New York: The Macmillan Company, 1937. Price: \$1.50.

It is a long contrast from ancient to modern alchemy which Rutherford makes in this little volume based on the Henry Sidgwick lecture which he gave at Newnham College, Cambridge, in November, 1936. No one was better equipped for this span than he who, together with Soddy, first proposed atomic disintegration as the explanation of radioactivity; also he who observed the first transmutation by bombarding nitrogen with alpha particles and in whose laboratory Cockcroft and Walton made the first transmutation by purely artificial means.

The various counting methods are described, the cloud chamber, the Van der Graaf and Lawrence high voltage machine, and the discovery of neutrons and positrons. The mass-energy transformation of Einstein is accepted as the basis of mass-energy relations in the nuclear reactions.

Although a net energy gain results from some nuclear reactions, the prediction is made that they will not prove an energy source of practical importance.

The bombarding reagents and the various types of nuclear reactions are briefly reviewed. X-rays of high energy have also been found effective in bringing about nuclear changes as Rutherford predicted a number of years ago.

S. C. LIND.

A Hundred Years of Chemistry. by ALEXANDER FINDLAY. 352 pp. New York: The MacMillan Company, 1937. Price: \$3.75.

The author needs no introduction to American chemists. His previous works in the field of physical and general chemistry are well known to our readers.

The present book might be regarded as a series of essays or chapters on the history of development in about a dozen different fields of chemistry more or less unrelated. His style is, as usual, clear and vivid. The choice of material is representative. Of course, it is a rather large undertaking to give an adequate survey of the hundred years of chemistry which covers nine-tenths or more of the whole, and yet do equal justice to all the fields. Naturally, a specialist in one of the various fields may be disappointed to find neglect of an important part of his subject. The reviewer, for example, thinks it unfortunate not to have included in the chapter on radioactivity something of the newer nuclear chemistry. By the use of the expression "excess positive charge of the nucleus" the author seems to believe still that there are free electrons in the nucleus. The conception of the neutron, of course, renders this assumption unnecessary, or even untenable.

A very welcome and unusual feature of the book is an appendix of twenty pages containing biographical notes regarding about sixty chemists mentioned in the text. A combined subject and author index is also provided.

S. C. LIND.

Glossary of Physics. By LEROY D. WELD. 255 pp. New York: The McGraw-Hill Book Company, 1937. Price: \$2.50.

This glossary contains some 2500 to 3000 definitions of terms, equipment, principles, equations, etc., used in the science of physics. The definitions are clear,

concise and up-to-date. Literature references are frequently given which greatly enhance its value. The arrangement is alphabetical. It is a valuable book of ready reference.

S. C. LIND.

Katalyse und Determinismus. Ein Betrag zur Philosophie der Chemie. By ALWIN MITTASCH. 14.5 x 22 cm.; ix + 203 pp. Berlin: Julius Springer, 1938. Price: 9.60 RM.

In this book Dr. Mittasch, who has in recent years written several very interesting books on the history of catalysis and on the rôle of catalytic phenomena in chemistry and biology, now enters the field of philosophy or, more correctly expressed, that of the philosophy of science. Starting with a discussion of the part played by catalysis in the "causation" of chemical phenomena (including especially the action of biocatalysts), the author soon proceeds to attack the wider general problems of determinism, causality, holism, and finalism in relation to all science. It would not be unfair to say that the main attack centers round the phenomena presented by living organisms.

From the hundreds of brief quotations interspersed throughout the text and the extensive bibliography, it is clear that Dr. Mittasch has read very widely in philosophical and biological literature and that his intention is to deal fairly with all shades of opinion. This embarrassment of riches, however, combined with a rather heavy literary style, makes the reading of the book somewhat difficult. One gathers that the author follows Planck and Einstein in holding to the principle of a "strict" causality. He adopts the "holistic" point of view so closely associated with the names of General Smuts and the late Professor Haldane, and sees in every "whole" (*Ganzheit*) a hierarchy of causes ("causalisms"), each of which possesses a determinate rank in the *Rangordnung* (order of ranking) of the whole, and all of which contribute to the causality of the whole." Thus, when we have to deal with living organisms, a place can be found for the "entelechia causalisms" postulated by Driesch, and especially for "psychical causalisms." That these causal factors cannot be pictured in time and space is no drawback, for, as the author points out, the same thing applies to the concepts of modern atomic physics. Moreover, as Bohr has so clearly indicated, the progressive advance of science must prepare us for a continuous development and widening of our concepts. Thus when we view the hierarchy of a living whole from "above downwards" or from "below upwards," the psychical-entelechia and the physicochemical descriptions may be regarded, not as contradictory, but as "complementary" in the sense of Bohr's principle of complementarity.

It would not be possible in a short review to do justice to Dr. Mittasch's learned discussion. Mathematicians, physicists, astronomers, and biologists have freely ventured to discuss the philosophy of science. It was time, as the author says, that a chemist took a hand in this game. With that opinion all chemists will surely agree, and we may certainly congratulate Dr. Mittasch on being led from meditations concerning the phenomena of catalysis to a brave attack on the dragons of philosophical doubt. Although the reviewer believes that progress in this direction is most likely to come from an application of the methods of mathematical analysis and symbolic logic to the statement of the problems, that is no reason why Dr. Mittasch should not follow the more usual method. Wisely perhaps, he nowhere attempts to define and distinguish what he means by causality, determinism, finalism, etc. But the results are somewhat disconcerting. Thus his "determinism" seems to involve "Plan" and "Ziel," whereas determinism as usually defined in-

volves nothing more than a determinate functional relation between the "before" and the "after," as measured or observed.

One final remark on the subject of causality. Has Dr. Mittasch ever read the sound criticism of David Hume?

F. G. DONNAN.

Abridged Scientific Publication from the Kodak Research Laboratories. Volume XVIII (1936). Rochester, N. Y.: The Eastman Kodak Company, 1937.

The eighteenth volume contains about sixty abridged papers condensed from the form in which they appeared in 1936 in about a dozen and a half different scientific periodicals. These papers are principally in the field of photography, optics, and spectroscopy, with some contribution to analytical and organic chemistry and to radiography.

S. C. LIND.

The Retardation of Chemical Reactions. By KENNETH C. BAILEY. 479 pp. New York: Longmans, Green and Company, 1937. Price: \$8.00.

For the past two decades the chemist has been learning that it is often as important to prevent reactions as to cause them. The discovery of chain mechanism, which put the subject on a scientific basis, has stimulated research and applications.

The author has covered the entire field mostly from the experimental viewpoint. After a brief historical survey he takes up the subject of oxidation, chain reactions, antioxidants, and oxidation of organic and inorganic substances in the gaseous, liquid, and solid states, to which more than half of the book is devoted.

Among applications he discusses the protection of rubber, the prevention of metallic corrosion, the setting of cement and plaster of Paris, antiknock action, the stabilization of hydrogen peroxide, decompositions of various types, the hydrogen-chlorine reactions, polymeric and isomeric changes, and a number of unclassified reactions. This subject cannot fail to be of interest both practically and theoretically to a wide circle of chemists. The author has made an excellent selection of experimental material, and has picked his way carefully through the maze of kinetic fact and fancy which fills the literature.

An extensive bibliography of 1630 references, which occupies nearly 100 pages and takes the place of an author index, doubtless has added materially to the cost of the book.

S. C. LIND.

The Fine Structure of Matter: Part I. X-rays and the Structure of Matter. By C. H. DOUGLAS CLARK. 216 pp. New York: John Wiley and Sons, 1937. Price: \$4.25.

This book is Part I of Volume II of *A Comprehensive Treatise on Atomic and Molecular Structure* being prepared by the author in a fashion somewhat similar to Mellor's monumental work in the field of inorganic chemistry. Works of this type are a great boon to the teacher and to the research investigator, and are very welcome additions to our scientific literature. It is not a book from which to study the subject in detail, but attempts to give a general outline of the field together with many references to the original literature. More than a thousand references, chiefly from the period 1928-1934, are given. For earlier references the reader is expected to consult Ewald and Hermann's *Strukturbericht*.

In the general preface the author points out his purpose to save space by frequent reference to summarizing works, and thereby to avoid repetition of the original

references quoted in them. It is surprising then to find only three additional books on the subject listed among the references. Such excellent books as Wyckoff's *Structure of Crystals* and its 1930-1934 *Supplement* might well have been mentioned for their important summaries of crystal structure results.

It is not quite clear why the references could not have been brought up to a later date than the end of 1934 in a book which did not appear off the press until late in 1937.

The common symbols of crystallography and crystal structure have been largely omitted from the list of symbols in the front of the book, but they have been used freely throughout the book. The first chapter, on crystal geometry and the methods of analysis, cannot be considered to have been adequately treated, but the rest of the material seems reasonably complete. For example, the atomic structure factor in the appendix has a list of 120 references. There are a few important omissions. The Weissenberg method is not mentioned, and the only reference to molecular rotation in solids is on page 103.

The book contains many excellent drawings of structures, but figures XI, XVII, and XXXV might well have been replaced with simpler diagrams. The reviewer doubts that much advantage was gained by the adoption of the symbols suggested on page 71. In fact, the author has not been wholly consistent in the use of his symbols, as is seen on pages 55, 56, and 86.

Errors of one kind or another inevitably creep into a work of this kind. Some of them noted by the reviewer are on pages 10, 15, 37, 71, and 119. A few simple typographical errors were also noted.

In conclusion, it is the reviewer's opinion that the book will serve a very useful purpose as a quick reference to the results of crystal analysis.

HAROLD P. KLUG.

Textbook of Thermodynamics. By PAUL EPSTEIN, Professor of Theoretical Physics, California Institute of Technology. xii + 406 pp.; 64 figs.; 14½ x 23 cm. New York: John Wiley and Sons, Inc., 1937. Price: cloth, \$5.00.

The author treats thermodynamics from the point of view of the physicist. He has designed his book to be used partly as a basic course for seniors and younger graduate students, and partly for reference or for courses given to more advanced students. The arrangement of the material is along the lines of the classical treatment. The book contains, however, much modern material and much that is of interest to the chemist. The author has departed from the notation which has become more or less standardized in this country. He deals with the fundamental concepts in a detailed and careful manner, and makes numerous applications in the realm of physics and chemistry. His concept of entropy is based upon the cyclical processes. Chapters are included dealing with electron and ion clouds, equilibrium involving radiation, magnetic and electric phenomena, and the limitations of thermodynamics, including the theory of fluctuations. The historical development of the first law is interestingly discussed in seven pages. The author follows the Nernst tradition and omits references to important American contributions to the field.

MERLE RANDALL.

Gmelins Handbuch der anorganischen Chemie. 8 Auflage. Herausgegeben von der Deutschen Chemischen Gesellschaft. System-Nummer 22: Kalium. Lieferung 4. Verbindungen bis Kaliumacetat. 26 x 18 cm.; pp. xxv + 805-932. Berlin: Verlag Chemie, 1937. Price: 15 RM.

The present section includes compounds of potassium with boron and carbon.

The boron compounds include borates, perborates, and borofluorides; the carbon compounds include carbides, carbonyls, carbonates (with their manufacture), carbamate, percarbonates, cyanide (with its manufacture), cyanate, thiocyanate, formate, and acetate. The perborates are treated as true per-salts. The carbonate is now largely made by the Engel-Precht process, depending on the decomposition of potassium chloride solution with magnesium carbonate, full details of the various modifications of which are given, but it is also produced by the action of carbon dioxide on electrolytic caustic potash. Full details of the properties of all the compounds are given, the recent literature being well covered, but the solubility of potassium thiocyanate in alcohol is omitted.

J. R. PARTINGTON.

Gmelins Handbuch der anorganischen Chemie. 8 Auflage. Herausgegeben von der Deutschen Chemischen Gesellschaft. System-Nummer 24: Rubidium. 26 x 18 cm.; pp. x + 250. Berlin: Verlag Chemie, 1937. Price: 31.50 RM.

The present volume constitutes a complete monograph on rubidium and its compounds. The compounds of rubidium are prepared from carnallite, and rubidium and cesium compounds from lepidolite. A method of preparation depends on the precipitation of cesium, but not rubidium, by antimony trichloride from solutions of the chlorides in hydrochloric acid. There has been a considerable fall in price of rubidium and cesium compounds since 1930. Pure rubidium is obtained by thermal decomposition of the azide. There is a section on analytical chemistry.

J. R. PARTINGTON.

Gmelins Handbuch der anorganischen Chemie. 8 Auflage. Herausgegeben von der Deutschen Chemischen Gesellschaft. System-Nummer 27: Magnesium. Teil B. Lieferung 1. Verbindungen bis Magnesium und Jod. 28 x 18 cm.; pp. vii + 200. Berlin: Verlag Chemie, 1937. Price: 23.25 RM.

Compounds of magnesium with hydrogen (MgH detected in band spectra only), oxygen, nitrogen (including oxy-compounds), and halogens (including oxy-salts) are described in a very thorough manner. The nitride is prepared by heating magnesium filings for 4 to 5 hours at 800-850°C. in pure nitrogen. The use of magnesium perchlorate as a drying agent for gases is described. The descriptions of the solubilities are accompanied by phase rule diagrams, and there are extensive tables of numerical data. Some of the sections are of considerable technical interest. The general feature of the whole treatise, viz., a full description of the physical chemistry of the materials described, is evident in the present volume, which will be of considerable interest to physical chemists.

J. R. PARTINGTON.

Legierungen der Platinmetalle. Patentsammlung. By G. A. GRÜTZNER AND C. GÖTZE. Anhang zu den System-Nummern 63 bis 68, Gmelins Handbuch der anorganischen Chemie. 8 Auflage. Herausgegeben von der Deutschen Chemischen Gesellschaft. 26 x 18 cm.; 536 pp. Berlin: Verlag Chemie, 1937. Price: 40.50 RM.

The uses of the platinum metals and their alloys have recently become increasingly important and there is a large patent literature. The present volume brings this together in a very convenient tabular form, the compositions and properties of the alloys being given briefly in a systematic order, with references to the patents. The treatment is very complete, and the book is therefore of considerable value and importance.

J. R. PARTINGTON.

Reports on Progress in Physics. Volume IV. Published by the Physical Society. 26 x 18 cm.; vi + 389 pp. Cambridge: The University Press, 1937. Price: 20s.

The present volume contains eighteen articles, those of particular interest to physical chemists being on the adsorption of gases on solids, surface tension, super-sonics, thermodynamics, the electronic charge, electrolytes, spectroscopy and some aspects of atomic physics, although nearly all the remaining articles contain more or less of general interest from the point of view of physical chemistry. The sections usually present enough background to make them intelligible and interesting, the abstract style being notably avoided in the better articles. In some cases, as in the section on electrolytes, the detailed presentation of well-known material, which can be found in textbooks, seems to the reviewer to have been overdone, to the exclusion of more recent developments, no mention at all of which is to be found. No modern presentation of the theory of electrolytes can be based on the simple theory of Debye and Hückel, as is done here, at least if the interests of physical chemists are to be considered. As in previous reports, there is a welcome tendency to include quantitative data, so that these volumes will, during the period of their youth, form useful supplements to tables of data. The paper, printing, and binding are of high quality.

J. R. PARTINGTON.

Thermodynamics. By E. FERMI. 23 x 16 cm.; x + 160 pp. London and Glasgow: Blackie and Son, Ltd., 1938. Price: 12s.6d.net.

This book is characterized by a very clear treatment of fundamental principles and their application to a restricted field of problems, especially chemical equilibria in gases and dilute solutions. Ideal systems only are considered. The two laws are treated in a very clear and satisfactory manner, the second law being developed in relation to Carnot's cycle through the efficiency of a reversible engine in the classical manner. This treatment can hardly be evaded if a real understanding of the matter is desired. The entropy and thermodynamic potentials are then carefully dealt with, irreversible changes being included. The chapter on thermodynamic potentials gives one of the very few deductions of the maximum work equation (called by the author the isochore equation) to be found in treatises on thermodynamics. The same remark may also be made about the deduction of the maximum work of a gas reaction in the following chapter, in which the external work term is correctly retained. In the chapter on dilute solutions Planck's treatment is essentially followed. The last chapter, on Nernst's theorem, contains a brief but valuable sketch of its relation to statistical methods, and, in view of recent criticisms of the theorem and the undoubted competence of the author in the field of statistics, it is interesting to note his conclusion that the theorem is generally valid. There are problems for exercise but no answers to them. Prof. Fermi's book would form a very useful supplement to some recent treatises in which the fundamentals of thermodynamics are dealt with in a sketchy manner, or entirely omitted, so that the real meaning of the subject is obscured and its applications become largely exercises in algebra or elementary calculus, a treatment which the author expressly avoids. The book may be recommended as a very clear and accurate introduction to the subject of thermodynamics.

J. R. PARTINGTON.

STUDIES OF THE MEASUREMENT OF THE ELECTRICAL CONDUCTIVITY OF SOLUTIONS AT DIFFERENT FREQUENCIES. VIII

OSCILLOGRAPH TESTS ON CONDUCTIVITY CELLS

S. F. ACREE,¹ EDWARD BENNETT, G. H. GRAY, AND HAROLD GOLDBERG

Department of Electrical Engineering, University of Wisconsin, Madison, Wisconsin

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I. INTRODUCTION

In collaborative work in 1915-16 at the University of Wisconsin, dealing with precision inductance and capacitance bridges and techniques for measuring the true electrolytic conductance and the "capacitance or condenser effect" exhibited at the electrodes of a conductivity cell at different frequencies, it was shown (13, 8, 14, 11; see also 16, 15, 17, 5, 6, 2, 10) by both bridge and oscillograph measurements at audio frequencies that, to a first approximation, cells with bright platinum electrodes have the electrical characteristics of a resistor, R , in series with a large capacitor, C , rather than the properties of a resistor in parallel with a capacitor. A second and closer approximation to the characteristics of the electrolytic cell is obtained by conceiving a high resistance leak, R_1 , to be connected across the terminals of the series capacitor of the first approximation, as illustrated in figure 1.

The features of the conductivity cell recognized at that time as of importance for further study are schematically illustrated by the arrangement of resistors and capacitors in the "artificial cell" or "simulating network" of figure 2.

In figure 2 the heavy lines of the two capacitors C_1 and C_2 represent the leads and platinum electrodes of the cell, and the + and - signs at their surfaces indicate the charges on the metal. The + and - signs back of the lighter lines of the capacitors C_1 and C_2 indicate charges in the layers of electrolyte adjacent to the electrodes. These charges in the electrolyte are the result of ionic migration and of elastic displacements within the molecular structures of the solution. In very precise approximations, outside the scope of this article, there is probably associated with C_1 and C_2 also the relation of transient and steady-state capacitance phenomena

¹ Present address: National Bureau of Standards, Washington, D. C.

to (a) the mechanism and rate of reversible deposition and discharge of the ions of the solute and solvent (e.g., H^+ and OH^- of water), (b) the behavior of fresh and aged optically flat, smooth, rough, and spongy electrode surfaces, in connection with the reversible deposition and discharge of ions, and association, union, and recharge of atoms and radicals, (c) the reversible segregation and re-deposition of ionic and colloidal particles of the electrode material, alone and electrically associated with other ions, and giving rise to alteration of the electrode surfaces, (d) oxidation and reduction of the ions and moles of electrolytes and non-electrolytes in solution and on the electrodes, (e) the amount, fate, and electrical and chemical

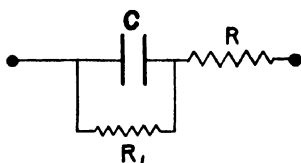


FIG. 1. Network simulating a conductivity cell. Second approximation to a conductivity cell.

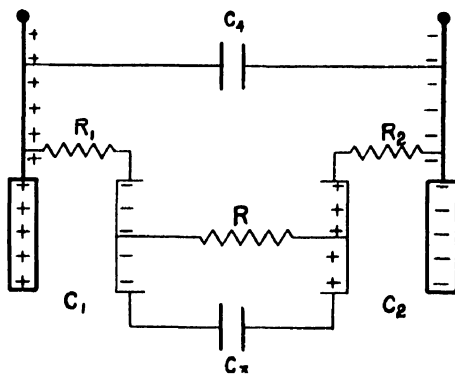


FIG. 2. Network simulating a conductivity cell. Third approximation to a conductivity cell.

character of gases deposited on the electrodes, (f) the activities of the pore walls and solutes causing adsorption of the solute and solvent, (g) electrical phenomena associated with the polarity, viscosity, electrophoresis, and internal structure of the solvents and solutes, particularly in such cases as solutions of metallic sodium in liquid ammonia, and (h) the capacitance due to the solvent alone as differentiated from that arising from the solute, and allowance for both the measured capacitance and conductance found for the solvent when making the usual solvent corrections in studies of the conductance-capacitance properties of electrolytes.

The capacitances of C_1 and C_2 were shown to have different values de-

pending upon the area, material, and surface character of each electrode, the degree of reversibility of the reactions at the two electrodes, and the types, mobilities, and activities of the solute ions. In the first approximation to the cell, the resultant capacitance of the two series capacitors C_1 and C_2 is treated as a single capacitance in series with the resistance R of the column of electrolyte between the electrodes.

The column of electrolyte between the electrodes may be thought of as made up of three portions: namely, the two layers of electrolyte each adjacent to one of the two electrodes, in which layers the concentration and composition of the electrolyte change throughout the current cycle, and the remaining portion of the column in which they do not change. It is readily seen that the actual resistance of the column of electrolyte varies throughout the current cycle. Moreover, its effective value averaged over the cycle will depend upon the frequency of the alternating current, since the lower the frequency, the greater will be the change in concentration in the electrode layers and the greater will be the depth of the layers which are affected by ionic migration. As the measuring frequency is made higher and higher, the changes in concentration over the cycle become less and less, and the measured resistance decreases and approaches the true ohmic resistance of an undisturbed column of electrolyte between the electrodes.

If a network simulating the electrolytic cell is to be made up of *fixed* resistances and capacitances, then the change with frequency of the measured resistance of the electrolytic cell can be closely (but not precisely) simulated by a network in which leaks R_1 and R_2 are connected in parallel with each of the capacitors C_1 and C_2 (or by a single leak, R_1 in figure 1, connected in parallel with the single capacitor whose capacitance is that of C_1 and C_2 in series). The ohmic resistances of the leaks R_1 and R_2 are high in comparison with the capacity reactances $1/(2\pi f C_1)$ and $1/(2\pi f C_2)$ of the respective capacitors. The electrical characteristics of such an arrangement are a third approximation to the characteristics of the actual cell.

To determine the additional elements which would have to be added to the simulating network of third-order approximation to make the network simulate the electrolytic cell with even greater precision, particularly at high frequencies, would require precision measurements over a wide range of frequencies. Undoubtedly a capacitor C_3 would be required in parallel with the resistance R to simulate better the effect of the elastic displacements within the molecular structures, and also a small capacitor C_4 between the cell terminals to represent the capacitance between cell leads.

In the earlier work these diagrams of the constitution of fixed element networks whose electrical characteristics were to simulate those of given electrolytic cells were deduced from bridge balances obtained on such cells

after all transient terms had vanished from the measuring current and the alternating current had attained its "steady state". This question naturally arose: Will the transient currents which flow in these simulating networks when they are connected to and disconnected from the source of alternating current simulate the transient currents which flow in the electrolytic cells when they are subjected to similar switching operations? To answer this question, oscillograms were taken (1916) to show the wave forms of the potential across electrolytic cells and the current through the cells for a number of cycles after the cells were switched on to the source of alternating current at different points on the potential wave form. These earlier oscillograms have recently (1935) been supplemented by others, showing the fall of the potential of the cells after they have been disconnected from the source at different points on the current wave form.

As no actual oscillograms covering these new phases of the theory of the electrode reactions and their relations to conductivity measurements have apparently been available heretofore (7, 9, 4, 3)², this article is presented as a step in our attempts to secure a clear understanding of the fundamental nature of the electrode phenomena and to perfect methods for the accurate measurement of the ohmic resistance of electrolytic solutions.

II. EQUIVALENCE BETWEEN THE ELECTROMOTIVE FORCES OF POLARIZATION AND OF A SERIES CAPACITOR

When a small alternating electromotive force is impressed upon a conductivity cell containing an electrolyte between bright platinum electrodes, the cell is found by bridge and oscillograph measurements to have the characteristics, not of a pure ohmic resistance, but of an ohmic resistance connected *in series* with a capacitor.

The capacitor effect arises from the alternating electromotive force which is set up in the layers of electrolyte immediately adjacent to the electrodes as the result of changes during each cycle in the ionic concentration in these layers. For a sinusoidal current through the cell, this layer E.M.F. is a sinusoidal E.M.F. which is 90 degrees in advance of the current; as a first approximation it corresponds with the E.M.F. which would be observed across a capacitor connected in series with a pure ohmic resistance equal to the ohmic resistance of the column of electrolyte between the electrodes. However, this correspondence holds only as long as the measuring current densities are so low that the layer E.M.F. is below the E.M.F. of polarization of the cell. At current densities well above these values, the layer E.M.F. is neither directly proportional to the current nor sinusoidal in form.

In the case of electrolytic solutions of good conductivity measured between bright platinum electrodes at frequencies of 1000 cycles or less, the

² See Holler (1), who used exploratory electrodes near the cell electrodes for studying electrode potentials, as suggested by us in 1916 (12).

fictitious or equivalent capacitances C_1 and C_2 in series with the resistance of the column of electrolyte play a far more important part in the interpretation of measurements of the phase relations and the electrical impedance of the cell than do the capacitances C_3 , paralleling the resistance R , and C_4 representing the capacitance between leads. Each of these four capacitances causes the sinusoidal current through the cell to lead the sinusoidal E.M.F. impressed upon the cell. But for some of our measurements the tangent of the angle of lead (at 1000 cycles per second) due to the series capacitance is about 45,000 times as great as the tangent of the angle due to the parallel capacitance.

That the interpretation of precision measurements on conductivity cells requires the consideration of this series capacitance effect (and the ionic phenomena to which it is due), as well as the parallel capacitance, was established by our earlier alternating current measurements at 250 to 4000 cycles per second with precision inductance and capacitance bridges to determine the relations concerning the true and apparent resistances, the equivalent series capacitance, the size, material, and surface condition of the electrodes, and the frequency and magnitude of the E.M.F. applied to the cell in the measurements.

This paper contains several sets of oscillograms which show the relations between the wave forms of an alternating current through a conductivity cell and that of the corresponding electromotive force across the cell for a number of cycles immediately following switching operations which close or open the circuit at different points on the wave form of the current. The oscillograms were taken with the first objective of determining the effect of the frequency and of the magnitude of the impressed electromotive force upon the apparent series capacitance of the cell and upon the wave shape of the current. A second objective was to determine whether the transient terms which occur in the current and the electromotive force across such a cell immediately after a switching operation which connects or disconnects a source of alternating electromotive force to the cell are, to a first approximation, identical in form with the transient terms which occur when identical switching operations are carried out upon a simulating network made up by connecting an appropriate resistor and capacitor in series. A third objective was to throw additional light on the nature of the "leak resistors" R_1 and R_2 of figure 2 by determining the rate of decrease of the cell E.M.F. when the cell is cut off from the source of current at the peak and zero points of the current, and is then allowed to discharge through resistors of different values.

III. METHOD AND APPARATUS

The oscillograms were obtained by means of a General Electric three-vibrator oscillograph with the circuit connections shown in figures 3 and 4. Referring to these figures: L and C represent an inductor and a capacitor

of such values as to filter out all harmonics from the E.M.F. wave form of the 60-cycle circuit. T is a multi-tap auto-transformer by means of which the desired E.M.F. can be impressed upon the cell. S represents a switch which by means of a synchronous motor can be closed and subsequently opened at any desired points of the wave form of the impressed electromotive

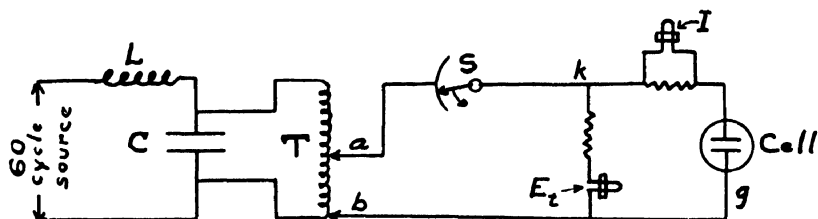


FIG. 3. Diagram of circuit for making oscillograms of wave forms of current and total impressed voltage. For the 240-cycle measurements wires a and b were connected to the secondary coil of the Vreeland oscillator.

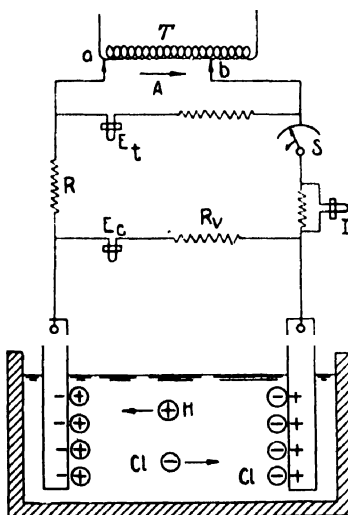


FIG. 4. Diagram of circuit for making oscillograms of wave forms of current, total impressed voltage, and E.M.F. impressed upon the conductivity cell. The signs on the electrodes indicate the charges on the electrodes. The condition is pictured for the end of the half-cycle in which the current has been flowing in the direction of the arrow A .

force. I represents the oscillograph vibrator which records the wave form of the current through the cell. In figure 4 the vibrator I records the total current taken by the cell and the vibrator E_c . The current taken by the vibrator E_c is only 3 to 8 per cent as great as that taken by the cell. E_c represents the vibrator which records the wave form of the E.M.F. impressed upon the cell. E_t represents the vibrator which records the wave form

of the E.M.F. impressed across the series consisting of the cell and any resistance in series with the cell. In figure 4 a resistance, R , was inserted in series with the cell for the purpose of increasing the time-constant of the circuit. On the films the three wave forms referred to above are marked I , E_c , and E_t , respectively.

Suitable interconnections between the shutter mechanism of the oscillograph and the tripping mechanism of the motor-operated switch, S , were provided so that the following sequence of events occurred in the exposure of a film: (1) The shutter of the oscillograph opened, thereby exposing the film to the light from the vibrators of the oscillograph. Since the switch, S , remains open for an interval of about $2/100$ of a second after the opening of the shutter, the vibrators trace on the film during this interval a short length (2 to 6 cm.) of the zero lines for current and voltage. (2) About $2/100$ of a second after the opening of the oscillograph shutter, the trigger on the switch, S , is tripped and the synchronous motor then closes this switch at the selected point on the succeeding cycle of the E.M.F. E_t impressed upon the circuit. For some of the sets of films the switch, S , was set to close first as above and then after 7 cycles to open at predetermined points on the wave form of the current. (3) The shutter of the oscillograph is automatically closed after the drum on which the film is mounted has made one complete revolution.

The electrodes of the conductivity cells used in all these tests were concentric cylinders of bright platinum spaced approximately 1 mm. apart. For the oscillograms listed in tables 1, 2, and 3, the cylinders were each 5.1 cm. long and the inner cylinder had an outside diameter of 1.3 cm. For the oscillograms described in section VII, the corresponding dimensions were 7.7 cm. in length and 2.5 cm. in diameter. Three different solutions were used, as specified later, namely 0.2 N sodium chloride, 1 N sulfuric acid, and 1 N hydrochloric acid.

Two frequencies were used,--- 60 (or 61) and 240 cycles per second. The 240-cycle current was obtained from a Vreeland oscillator and the 60-cycle current from the local city service.

IV. FILM DATA FOR THE STEADY STATE:—EFFECT OF IMPRESSED VOLTAGE AND FREQUENCY

With the connections shown in figure 3, the voltage of the source was adjusted to the desired values and a series of oscillograms was taken with different impressed voltages and at the two frequencies, 61 and 240 cycles per second. For this series of films the solution in the cell was 0.2 N sodium chloride.

Figures 5, 6, 7, 8, and 9 (films 7, 8, 9, 10, and 11, respectively) are typical of this series. From these films the data compiled in tables 1 and 2 were obtained in the manner described below.

The magnitudes of the current and the voltage and the angle by which the current wave leads the voltage wave (designated as the phase angle) were obtained from measurements made on the films. The capacitance, the resistance, and the phase angle of the cell itself were then computed as follows:

- Let E represent peak voltage (determined from oscillogram),
 I represent peak current (determined from oscillogram),
 θ represent the angle by which the sinusoidal current leads the sinusoidal voltage as measured on the oscillograms,
 X_c represent the equivalent series capacitive reactance of circuit k-g-d (figure 3), and
 R represent resistance of circuit k-g-d (figure 3).

Then

$$X_c/R = \tan \theta \quad (1)$$

The impedance Z of the circuit k-g-d (figure 3) is then

$$Z = E/I \quad (2)$$

and on the assumption that the capacitance of the cell is in series with its resistance,

$$R = Z \cos \theta \quad (3)$$

$$X_c = Z \sin \theta \quad (4)$$

The capacitance C of the cell in farads is

$$C = \frac{1}{2\pi f X_c} \quad (5)$$

The resistance of the cell itself (R_c) is found by subtracting from R the resistance of all parts of the circuit external to the cell between points k and d. The values of the external resistance and of the cell resistance are given in tables 1, 2, and 3 in the columns headed "External resistance" and " R_c ", respectively.

The true phase angle θ_c of the cell is then

$$\theta_c = \arctan X_c/R_c \quad (6)$$

and the true voltage impressed on the cell is

$$E_c = I\sqrt{R_c^2 + X_c^2} \quad (7)$$

The values of the peak current, the peak voltage, and the phase angle of the cell were determined from measurements made on the last cycles recorded in the films. The transient terms in the current, the presence of which can be detected in the current during the first half-cycle, become of negligible magnitude within 1/60 of a second after the closing of the switch. These transient terms will be discussed later.

Tables 1 and 2 contain the results of the measurements made on the films.

V. DISCUSSION OF THE TABLES AND OF THE FILMS

No high degree of accuracy should be attached to the numerical values for the cell resistance and capacitance appearing in the tables. All these values were computed from measurements of rather short lengths. In

TABLE 1

Effect of impressed voltage on the characteristics of the cell containing 0.2 N sodium chloride

(Figure 3 connections)

FILMS	FRE- QUENCY	EXTER- NAL RE- SISTANCE	LAST CYCLE			E_c	R_c	X_c	C	θ_c
			Peak volts	Peak amperes	Lead angle					
		ohms			degrees	volts	ohms	ohms	μf	degrees
7	61	0.102	0.665	1.48	42	0.565	0.233	0.301	8700	52
8	61	0.017	1.95	5.90	32	1.86	0.263	0.175	14900	33
9	61	0.017	3.33	10.5	25	3.17	0.270	0.134	19500	26
10	61	0.017	4.33	15.1	20	4.10	0.253	0.098	26700	21
11	61	0.017	7.70	31.2	13	6.90	0.214	0.056	46700	15

TABLE 2

Effect of frequency on the characteristics of the cell containing 0.2 N sodium chloride

(Figure 3 connections)

FILMS	FRE- QUENCY	EXTER- NAL RE- SISTANCE	LAST CYCLE			E_c	R_c	X_c	C	θ_c
			Peak volts	Peak amperes	Lead angle					
		ohms			degrees	volts	ohms	ohms	μf	degrees
14	239	0.094	0.152	0.44	17	0.113	0.237	0.101	6600	23
15	240	0.103	0.805	2.30	20	0.589	0.226	0.120	5520	28
16	244	0.104	1.30	3.76	16.5	0.931	0.227	0.098	6670	23
17	61	0.094	0.165	0.31	45	0.146	0.282	0.376	6950	53
18	61	0.101	0.62	1.24	48	0.545	0.234	0.372	7020	58
19	61	0.104	1.29	2.70	43	1.10	0.246	0.327	8000	53

some cases an error of 0.01 cm. in the measurement of an amplitude or phase angle would result in an error of 4 per cent in the computed values. The oscillograms were not taken with the idea of making precise determinations of the resistance and capacitance of the cell, but rather to examine the transient effects. The capacitance and resistance values are, however, of the same order as those found in our precision a.c. bridge measurements.

The tables indicate that the equivalent capacitance of the cell is approximately independent of the frequency and of the magnitude of the

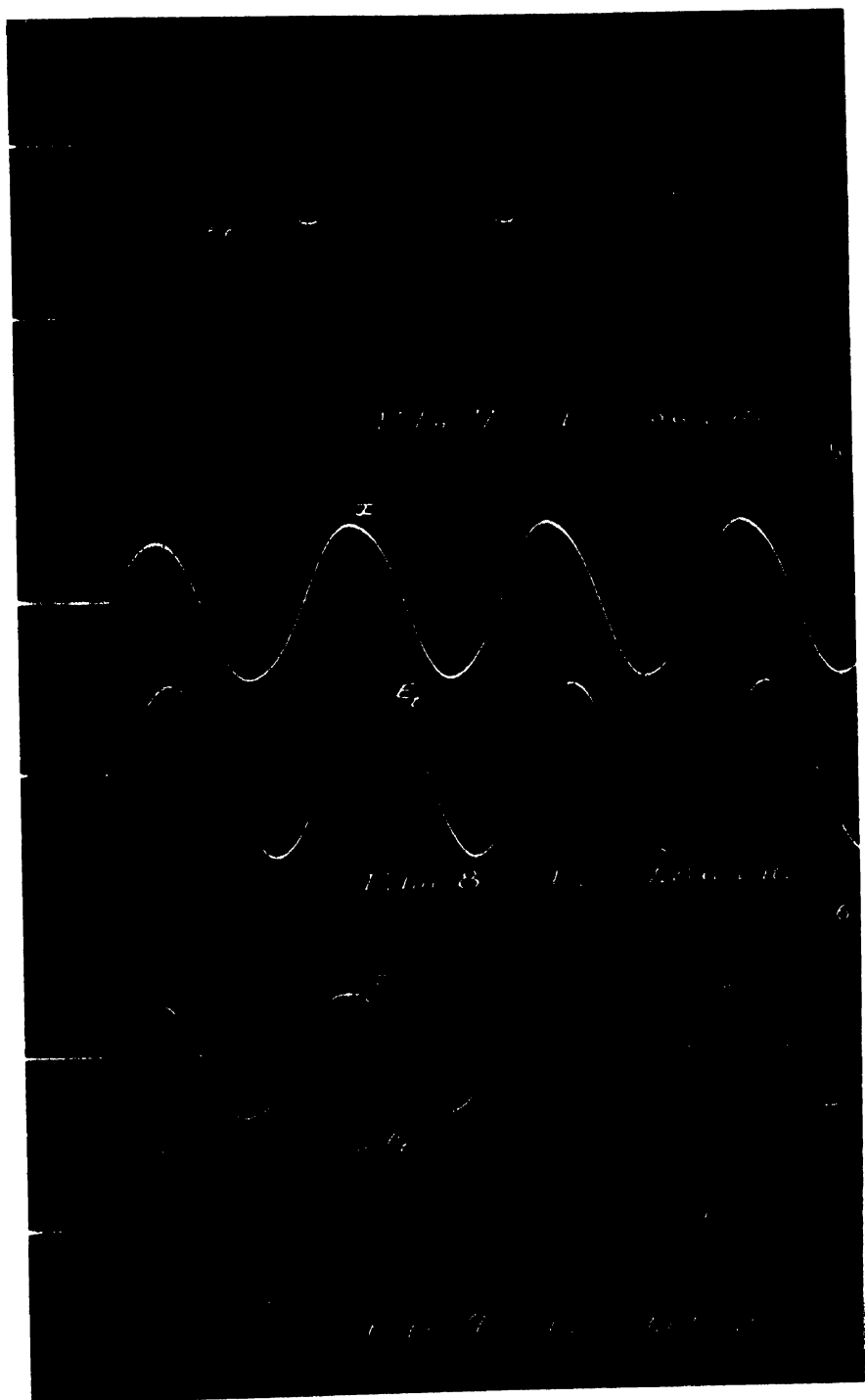
impressed E.M.F. if the latter is less than the E.M.F. of polarization of the cell. The equivalent capacitance of the cell increases with rise in the impressed E.M.F. above the E.M.F. of polarization and is roughly proportional to the rise. The results agree with our precise A.C. bridge measurements.

It should be recognized that this statement with reference to the equivalent capacitance at electromotive forces greater than the E.M.F. of polarization is a very loose one. The cell really has no *equivalent capacitance* for an impressed E.M.F. greater than the E.M.F. of polarization, because at these higher E.M.F.'s the oscillograms show that the cell no longer has the properties of a resistance connected in series with a capacitor. Compare, for example, the sine wave form of the current in figure 5 (film 7), which was taken at the impressed E.M.F. of 0.565 volt, with the distorted current wave forms of figures 6, 7, and 8 (films 8, 9, and 10), which were taken at 1.86, 3.17, and 4.1 volts, respectively. Film 8 (figure 6) is flattened on the left side of the I wave form with its peak shifted to the left, film 9 (figure 7) is flattened on top with its peak shifted downward, and film 10 (figure 8) is flattened on the right side with its peak shifted to the right. These differences are most easily observed by superimposing films 8, 9, and 10 (figures 6, 7, and 8). When the last cycle of film 10 (figure 8) was cut off, reversed, and superimposed on the preceding cycle a shift of the I peak to the right was clearly disclosed. This newly discovered "polarization peak-shift effect" must be associated with electrode reactions other than ion segregations and will be studied by scaling the heights and areas (and their differences) on both sides of the peaks of the wave forms to correlate these data with other polarization phenomena. For example, in film 10 (figure 8) the area of the portion of the current half-cycle lying to the right of the peak is roughly 10 per cent less than on the left. It is further noted in films 7 to 11 (figures 5 to 9) and in table 1 that with rise of the electrode potential E_e from 0.56 to 6.9 volts and of the apparent capacitance from 8700 to 46,700 microfarads, the transient terms decrease and the ratios of the heights of the peaks of the first and third current half-cycles are respectively about 0.77, 0.79, 0.86, 0.90, and 0.95. If the apparent electrode capacitance were constant above polarization voltage no such change should occur. A consideration of the phase relations between the current, the electromotive force expended in the resistance, and the electromotive force arising from changes in ion concentrations at the electrodes during

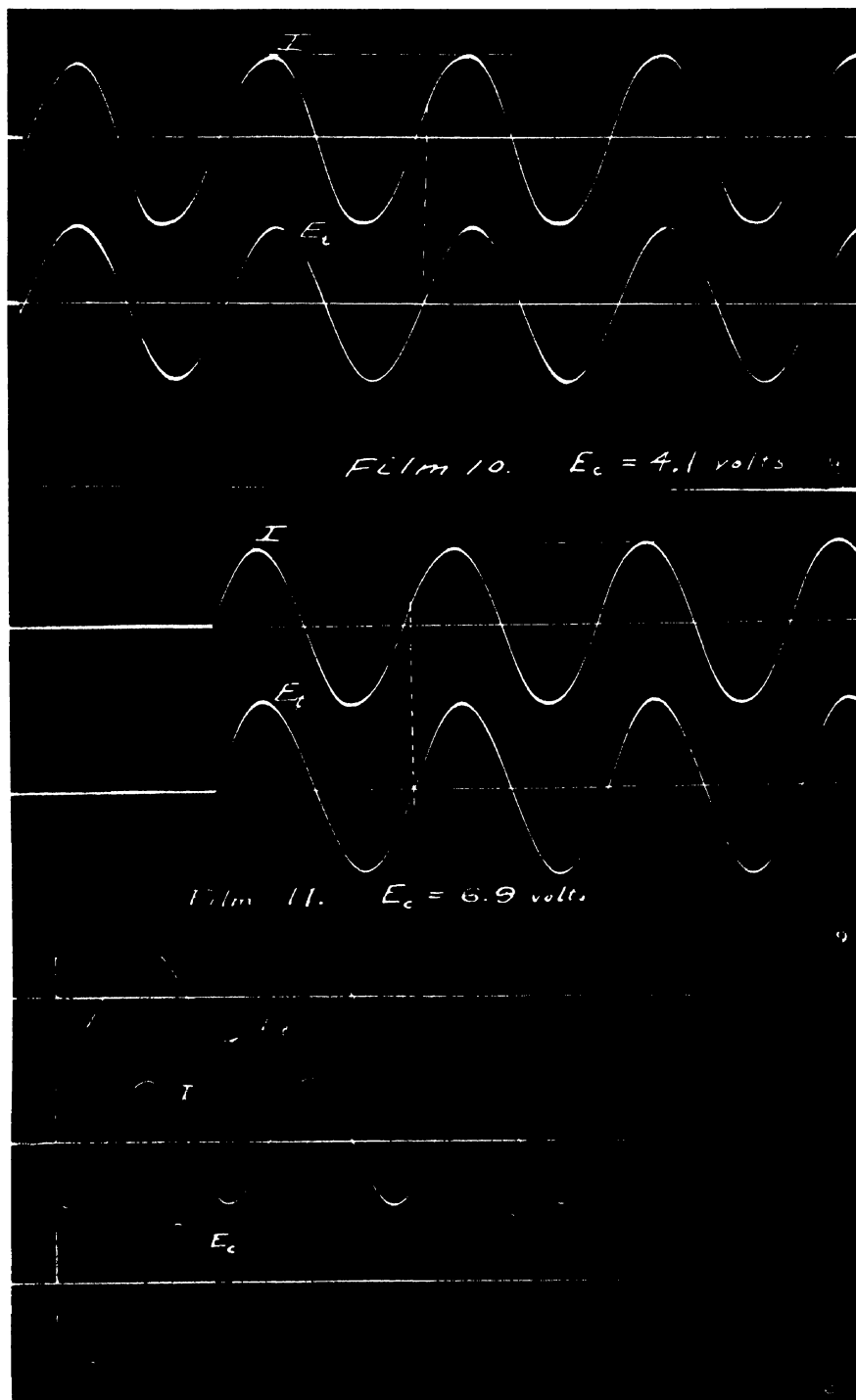
FIG. 5. Wave forms of applied voltage (E_e) and current (I) with 0.56 volt (E_e) across the cell. The current wave form was not distorted.

FIG. 6. Wave forms of applied voltage (E_e) and current (I) with 1.86 volts (E_e) across the cell. The current wave form was slightly distorted.

FIG. 7. Wave forms of applied voltage (E_e) and current (I) with 3.17 volts (E_e) across the cell. The current wave form was very much distorted.



FIGS. 5-7



FIGS. 8-10

the cycle leads to the prediction of a flattening of the current wave form at voltages somewhat in excess of the E.M.F. of polarization, which may be seen most clearly in figure 7 (film 9). Under impressed electromotive forces greatly in excess of an E.M.F. of polarization, the current wave form will again approximate the sine wave form because of the fact that the E.M.F. expended in the resistance is many times the E.M.F. of polarization (see columns headed " R_c " and " X_c ", table 1); therefore the latter will have little influence on the wave form of the current. This conclusion is borne out by a comparison of figures 7 and 9 (films 9 and 11) taken at 3.17 and 6.9 volts, respectively. In the latter film the distortion of the current wave form is not as marked as in the former. Film 7 (figure 5), taken at an impressed E.M.F. of 0.565 volt at 61 cycles, shows no distortion of the current wave form.

VI. TRANSIENT PHENOMENA IMMEDIATELY AFTER THE START OF AN ALTERNATING CURRENT THROUGH A CONDUCTIVITY CELL

The closing of the switch S in figure 3 suddenly impresses an alternating E.M.F. between the points k and d . This E.M.F. is recorded by the vibrator E_t while the current through the conductivity cell is recorded by the vibrator I . We may write the complete expression for the current which will flow through the cell under the impressed E.M.F. upon the assumption that the cell may be simulated by a capacitor having a capacitance of C farads in series with a resistor having a resistance R equal to the resistance R_c of the cell plus the resistance of the shunt and the current vibrator I .

If the equation for the impressed E.M.F. across k - g - d is

$$e_t = E \cos \omega(t - t_1) \quad (8)$$

the equation for the current, i , through the cell is

$$i = \frac{E}{\sqrt{R^2 + X^2}} \cos \left[\omega(t - t_1) + \arctan \frac{X}{R} \right] + \frac{E_d}{R} \exp \left(- \frac{t}{RC} \right) \quad (9)$$

in which time, t , is measured from the instant at which the switch closes, t_1 represents the interval from the instant of closing to the nearest positive peak of the impressed E.M.F., ω represents $2\pi f$, X represents $1/C\omega$, and

$$E_d = \frac{EX}{\sqrt{R^2 + X^2}} \sin \left[\omega t_1 - \arctan \frac{X}{R} \right] \quad (10)$$

FIG. 8. Wave forms of applied voltage (E_t) and current (I) at 60 cycles with 4.1 volt (E_c) across the cell. The current wave form was slightly distorted.

FIG. 9. Wave forms of applied voltage (E_t) and current (I) with 6.9 volts (E_c) across the cell. The current wave form was barely distorted.

FIG. 10. Wave forms of applied voltage (E_t), current (I), and E.M.F. (E_c) across the cell. When the switch was closed at peak E_t there was no noticeable transient effect in E_c .

The expression for the current contains two terms, the steady-state or sinusoidal term, and the transient or exponential term. The *damping constant* of the exponential term is $(-1/CR)$, and its *time-constant* is CR . In any interval of time (after the closing of the switch) equal to the time-constant, or equal to CR seconds, the exponential term decreases to $1/e$ th (36.8 per cent) of its initial value, and in an interval equal to 4.6 times the time-constant it decreases to 1 per cent of its initial value, or is negligibly small.

For the oscillograms taken with the figure 3 connections, of which films 7 to 11 are typical, the value of the time-constant was quite small, namely, 0.003 second or less. Consequently for these films the exponential term decreased to less than 1 per cent of its initial value in the first cycle after the closing of the switch. On the above set of films, the effect of the exponential term can be detected to best advantage in film 7 (figure 5). The low value of the first current peak on this film is due to the presence of the transient term.

In order to increase the time-constant of the transient term so that its value could be measured by scaling peak values over a number of cycles, the resistance of the circuit was now increased by inserting an additional resistance R of from 10.4 to 23.2 ohms, as shown in figure 4. Additional oscillograms were then taken upon the same conductivity cell as before, containing, however, 1 *N* sulfuric acid as the electrolyte. These oscillograms were all taken at a frequency of 60 cycles per second. Films 23, 24, and 25 (figures 10, 11, and 12) are typical. The data for these oscillograms are given in table 3.

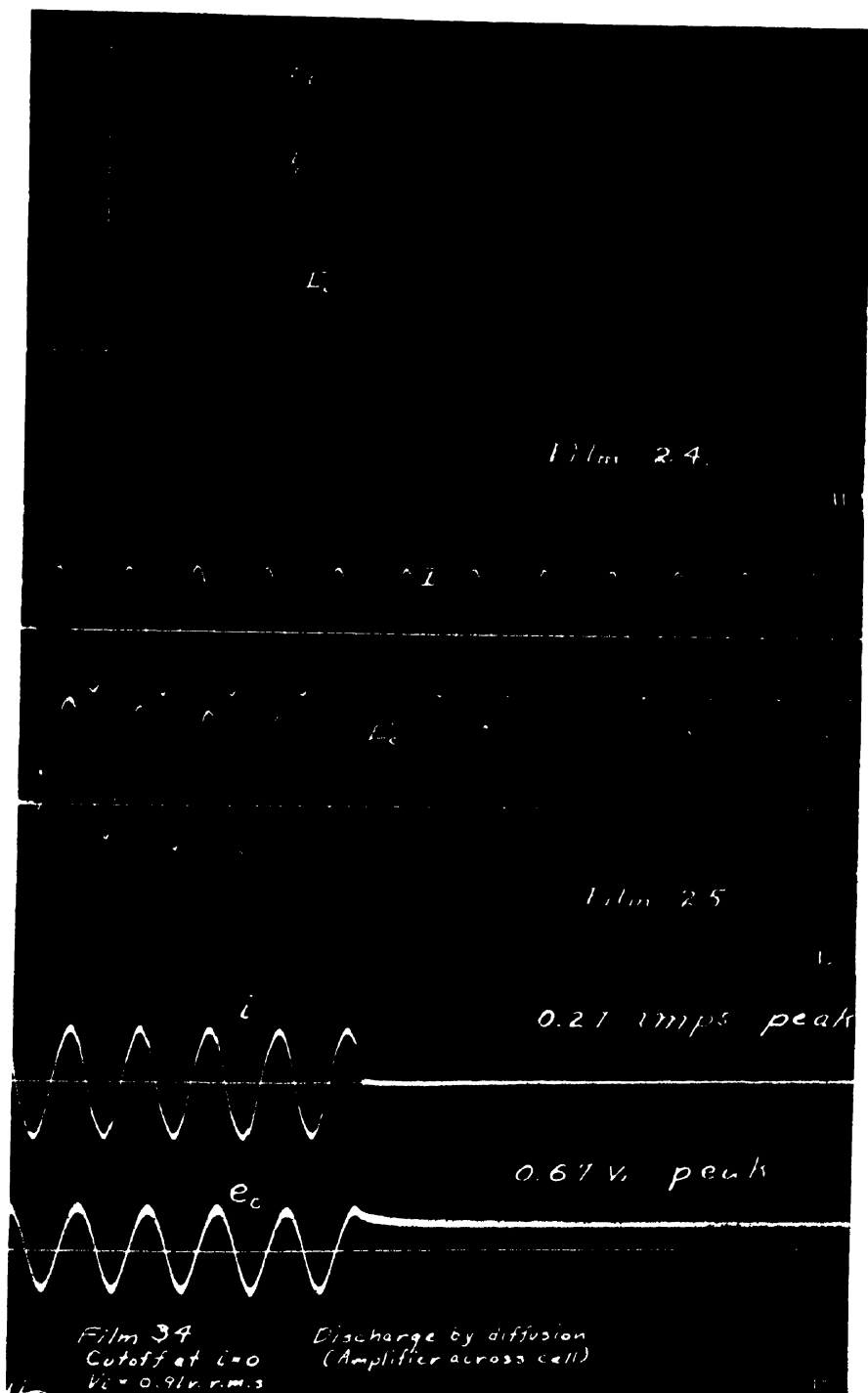
The figure 4 network containing the conductivity cell is simulated to a first approximation by the artificial network shown in figure 13. In this figure the capacitance C and series resistance R_s replace the conductivity cell of figure 4, and the values assigned to C and R_s are to be computed by the method described for tables 1 and 2. These computed values are given in table 3.

The general equations for the current through the oscillograph vibrator I and for the electromotive force impressed on the cell, as measured by the vibrator E_c , have been derived in literal form. From these involved literal

FIG. 11. Wave forms of applied voltage (E_i), current (I), and E.M.F. (E_c) across the cell. When the switch was closed at zero E_i the large transient effect observed in E_c continued for more than 4 cycles.

FIG. 12. Wave forms of current (I) and E.M.F. (E_c) across the cell. When the switch was closed at zero E_i a large transient effect was observed in E_c with a drift to steady state in about 10 cycles (0.16 second).

FIG. 15. Wave forms of applied voltage (E_i), current (I), and E.M.F. (E_c) across the cell. When E_i and I in the steady state were cut off at zero values and there was ion segregation at the electrodes, E_c decreased very slowly (time-constant greater than 48 seconds) when the cell discharged (electrodes attached to amplifier).



FIGS. 11, 12 AND

equations we have computed the numerical expressions for the current shown by the vibrator I and for the E.M.F. shown by the vibrator E_c for two cases; namely, (a) for the case in which the switch is closed at the zero of the E.M.F. across E_t , and (b) for the case in which the switch is closed at the peak of the E.M.F. across E_t .

If the switch is closed at the zero of the E.M.F. across E_t (as in figures 11 and 12) and if time is measured from the instant of closure of the switch S,

TABLE 3

Effect of transient terms on the characteristics of the cell containing 1 N sulfuric acid
(Figure 4 connections)

FILMS	FRE- QUENCY	EXTER- NAL RE- SISTANCE	LAST CYCLE			E_c	R_c	X_c	C	θ_c
			Peak volts	Peak amperes	Lead angle					
		ohms				volts	ohms	ohms	μf	degrees
23	60	10.4		1.63		0.52	0.147	0.285	9300	60
24	60	23.2		1.6		0.48	0.118	0.279	9500	67
25	60	23.2		1.6		0.50	0.081	0.302	8800	75

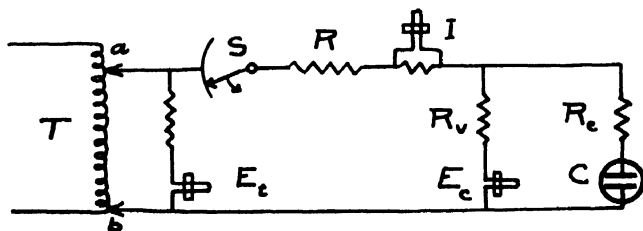


FIG. 13. Diagram of networks simulating figure 4

the equations for the figure 13 network used in obtaining film 24 (figure 11) are computed to be as follows:

For the total impressed E.M.F. as recorded by the vibrator E_t ,

$$i = E_1 \sin \omega t \quad (11a)$$

For the current as recorded by the vibrator I,

$$i = 0.01 E_1 [4.35 \sin (\omega t + 0.7^\circ) + 0.0019 \exp (-at)] \quad (12a)$$

For the E.M.F. across the artificial cell as recorded by the vibrator E_c ,

$$e_c = 0.01 E_1 [1.28 \sin (\omega t - 64.7^\circ) + 1.16 \exp (-at)] \quad (13a)$$

The value of the damping constant, a , appearing in the exponential factor, $\exp (-at)$, is given by the expression

$$a = \frac{1}{C \left[R_c + \frac{RR_v}{R + R_v} \right]} \quad (14)$$

On the other hand, if the switch S is closed at the positive peak of the E.M.F. across E_i (as in figure 10) the corresponding equations for the figure 13 network used in obtaining film 23 (figure 10) are

$$e_i = E_2 \cos \omega t \quad (11b)$$

$$i = 0.01 E_2 [9.44 \cos (\omega t + 1.5^\circ) + 0.013 \exp (-at)] \quad (12b)$$

$$e_e = 0.01 E_2 [2.98 \cos (\omega t - 59.4^\circ) + 0.14 \exp (-at)] \quad (13b)$$

An examination of these equations will show that the insertion of the resistance R (having a value 70 to 200 times as great as the resistance R_c of the cell) has had the following effects: (a) The time-constants of the exponential terms as computed from equation 14 are found to be 0.049 second for film 23 (figure 10), 0.0688 second for film 24 (figure 11), and 0.0634 second for film 25 (figure 12). Within the limits of the experimental errors the value of the time-constant computed from equation 14 checks with the experimentally determined value obtained by scaling the peak values of the curve E_e of film 25 (figure 12). (b) An inspection of equations 12a and 12b for the current i shows that the insertion of the resistance R has reduced the initial value of the transient term in the current to less than 0.5 per cent of the peak values of the steady-state alternating current. This conclusion is supported by the films, since an examination of the current curves on films 23, 24, and 25 (figures 10, 11, and 12) shows that the magnitude of the exponential term is so slight that it cannot be detected. (c) An examination of the equations from which were derived 13a and 13b for the voltage e_e across the conductivity cell shows that the exponential term in e_e will be a maximum if the switch closes at the instant corresponding to the zero point of the steady-state current through the cell, and will be zero if the closure occurs at the instant corresponding to the peak of the steady-state current through the cell. For the circuit used in obtaining films 23, 24, and 25 (figures 10, 11, and 12), these instants correspond very closely to the zero point and the peak of the impressed E.M.F. e_i .

In the case of films 24 and 25 (figures 11 and 12), the switch S closed substantially at the zero of the impressed voltage e_i . The large effect of the exponential term on the voltage E_e across the cell is quite evident. In the case of film 23 (figure 10), the switch S closed slightly before the peak of impressed E.M.F. E_i . The exponential term in E_e can barely be detected on this film, and the observable effect is to be attributed to the fact that the switch closed some degrees before the peak of the E.M.F. E_i . These three films are in general agreement with the equations 13a and 13b.

The physical reason (see figure 14) for the extremely small magnitude of the transient terms in the case of film 23 (figure 10), is as follows: In the steady state of a cell carrying an alternating current, the difference in the concentrations of the positive and negative ions at each electrode (figure 14, A and E) is zero at the instant when the current has its maximum

value and is a maximum (figure 14, D and F) at the instant when the current passes through the zero value. Consequently if the switch is closed at the instant when the current should have its maximum value, and if the inductance of the circuit is so low that the current can rise almost instantaneously to its normal peak value (as in film 23 (figure 10)), the cell attains practically at once (see below) the combination of values which characterizes the steady state, namely, peak value of impressed electromotive force (upon the entire circuit) in conjunction with peak value of current and zero difference of concentrations of positive and negative ions at the electrode. Under these conditions there will be no noticeable gradual drift from an initial combination of conditions to another corre-

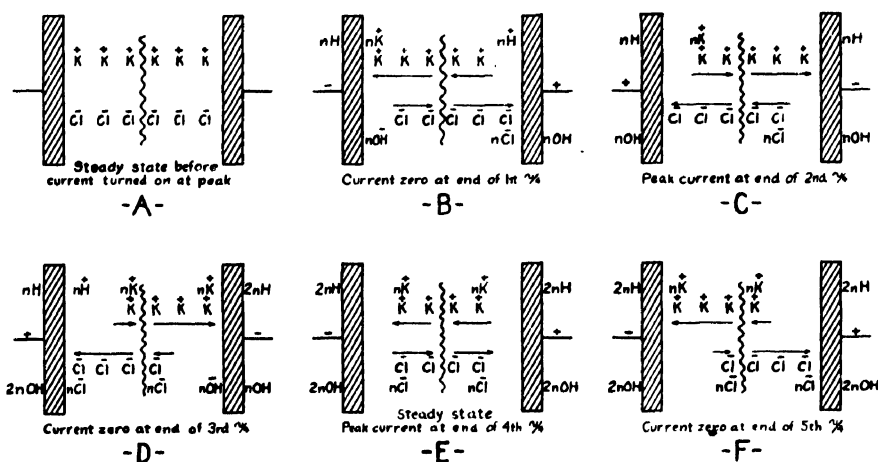


FIG. 14. Ion segregation and discharge at the electrodes during quarter-cycles

sponding to the steady state in the cell, and consequently there will be no appreciable transient terms in the electromotive force across the cell.

On the other hand, if the switch is closed at the zero point on the electromotive force wave form, at which in the steady state the current is zero and the difference in the concentrations of the two ions at the electrode is a maximum, then, during the *whole* of the succeeding half-cycle, the current will cause a change in concentration in one direction. In contrast to this, in the steady state, during the first half of the succeeding half-cycle (first quarter-cycle) following the point of zero current, the current reduces the difference in concentrations of the two ions from a maximum to zero, and then during the second half of the half-cycle builds up the difference in concentrations from zero to a maximum in the opposite sense.³ Conse-

³ It is planned to study the E.M.F. and capacitance at each electrode in relation to the transference numbers of the ions by means of A.C. potentiometer and oscillograph methods. For details of these phases see reference 13, pp. 2417, 2425, 2427, 2428, 2430.

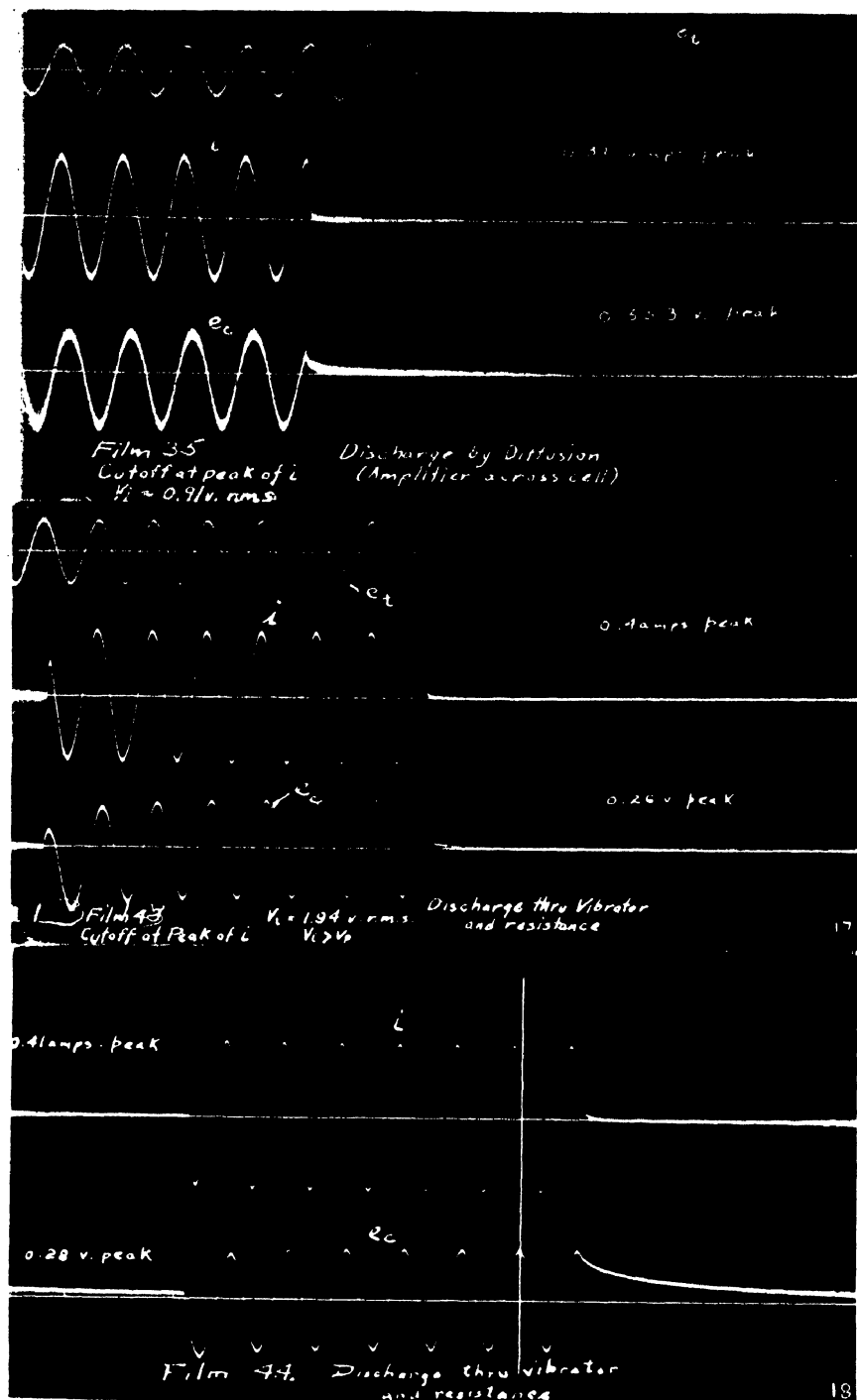
quently, in the first half-cycle following the closing of the switch at the zero point of the impressed electromotive force wave corresponding in the steady state to zero current, the *difference* in ionic concentrations at the electrodes builds up to approximately *twice* its normal or steady-state maximum value, and the E.M.F. of polarization builds up to approximately twice its normal value. The drift from the relations pictured for the first half-cycle to the symmetrical steady-state relation arises from the fact that the unsymmetrical E.M.F. of polarization subtracts unsymmetrically from the impressed electromotive force during its succeeding positive and negative half-cycles. This results in a slight lack of symmetry in the current about the line of zero current. The lack of symmetry is such as to cause the cycle of concentration values to drift exponentially from the initial cycle, namely 0, p , $2p$, p , 0 to the steady-state cycle, namely $-p$, 0, $+p$, 0, $-p$.

The electrical and ionic phenomena in the first cycle after the closing of the switch at the exact peak of the impressed E.M.F. will receive attention, because in certain cases the electrode reactions may not be completely symmetrical and reversible. Figure 14 illustrates the changes in the electrode double layers of electrolytes like potassium chloride, whose ions have substantially the same mobilities. In the first quarter-cycle n layers of $+$ and $-$ ions are moved to, and discharged at, the cathode and anode, respectively, with attendant discharge of n H^+ and OH^- ions from water. Steady-state conditions of concentration and discharge of ions at the two electrodes are not reached at peak current at the end of the second quarter-cycle but are obtained at the peak of the fourth quarter-cycle. Hence very small transient effects may be found within the first cycle, with steady-state conditions thereafter, especially by use of the methods described in the next section.

VII. TRANSIENT PHENOMENA UPON DISCONNECTING THE ALTERNATING CURRENT SOURCE FROM THE CONDUCTIVITY CELL

The synchronous switch S of figure 13 was now arranged to close and then, after an interval of slightly less than 7 cycles, to open again. The set of oscillograms in figures 15, 16, 17, and 18 (films 34, 35, 43, and 44, respectively) was then taken (1935) to show the transient effects which follow the opening of the switch at the two extreme points on the wave form of the 60-cycle current through the cell—namely, at the peak and at the zero point of the current. For these oscillograms a 1 *N* hydrochloric acid solution was used in the cell.

Upon closing the synchronous switch S, the equivalent capacitance of the cell is supplied through the resistance R. For these oscillograms this resistance was reduced to 4.7 ohms; at this value the time-constant of the



FIGS. 16-18

circuit was roughly 1 period of the 60-cycle circuit. This means that the transient terms in the polarization E.M.F. associated with the closing of the switch all reduce to zero before the opening of the switch, which occurred 7 periods later.

After the opening of the switch S, the E_c 10.3-ohm voltage vibrator branch was left connected across the cell for films 43 and 44 (figures 17 and 18). For films 34 and 35 (figures 15 and 16) the 10.3-ohm voltage vibrator branch of figure 13 was replaced by a vacuum tube voltage amplifier, which supplied the vibrator E_c but represented an impedance in excess of 10,000 ohms to the discharge of the cell through it.

To aid in the interpretation of these films, figure 19 has been drawn. This figure shows the relations between a sinusoidal current (I) through a conductivity cell (or rather through a simulating network consisting of a series combination of a resistor and capacitor having a resistance and a capacitive reactance corresponding to those of the actual cell) and the three sinusoidal electromotive forces associated with the current: namely, the E.M.F. (E_r) equal to $R_c i$, which is impressed upon the resistance R_c of the column of electrolyte; the E.M.F. (E_x) impressed upon the capacitor, or counteracting the E.M.F. of polarization; and the E.M.F. (E_c) impressed across the terminals of the cell, which is the sum of E_r plus E_x .

The E.M.F., E_x , across the regions of polarization (or across the capacitor) is seen to lag the current by 90° , while the E.M.F. across the resistance of the cell is seen to be in phase with the current. Consequently when, as in films 43 and 35 (figures 17 and 16), the synchronous switch S interrupts the sinusoidal supply current at its peak value (the instant t_p in figure 19), the E.M.F., E_c , across the cell at once drops to zero. It does this because at this instant there is no segregation of ions at the electrodes, or the E.M.F. of polarization, E_x , is zero, and the E.M.F. of resistance across R_c drops to zero when the current drops to zero.

On the other hand when, as in films 44 and 34 (figures 18 and 15), the switch S interrupts the supply current at the zero point (the instant T_0 in

FIG. 16. Wave forms of applied voltage (E_t), current (I), and E.M.F. (E_c) across the cell. When E_t and I in the steady state were cut off at peak values and there was no ion segregation at the electrodes, E_c dropped at once to zero value (electrodes attached to amplifier).

FIG. 17. Wave forms of applied voltage (E_t), current (I), and E.M.F. (E_c) across the cell. When E_t and I in the steady state were cut off at peak values and there was no ion segregation at the electrodes, E_c dropped at once to zero value (electrodes attached to E_c vibrator, figures 4 and 13).

FIG. 18. Wave forms of applied voltage (E_t), current (I), and E.M.F. (E_c) across the cell. When E_t and I in the steady state were cut off at zero values and there was ion segregation at the electrodes, E_c dropped to 36.8 per cent in about 0.05 second when the cell discharged (electrodes attached to E_c vibrator in figures 4 and 13).

figure 19), the E.M.F., E_o , across the cell apparently⁴ undergoes no abrupt or discontinuous change in value. At the instant t_0 the entire E.M.F. across the cell is associated with the segregation of ions indicated in figures 4 and 14 F. For the entire half-cycle preceding t_0 , the migration of the hydrogen and chloride ions has been in the directions indicated by the arrows in figure 4, and the concentration of hydrogen ions adjacent to one electrode and of chloride ions adjacent to the other attains a maximum at the instant t_0 . Upon the opening of S the two charged platinum electrodes start to discharge through the resistance of the branch containing the voltage vibrator E_o . As the charges on the platinum electrodes decrease,

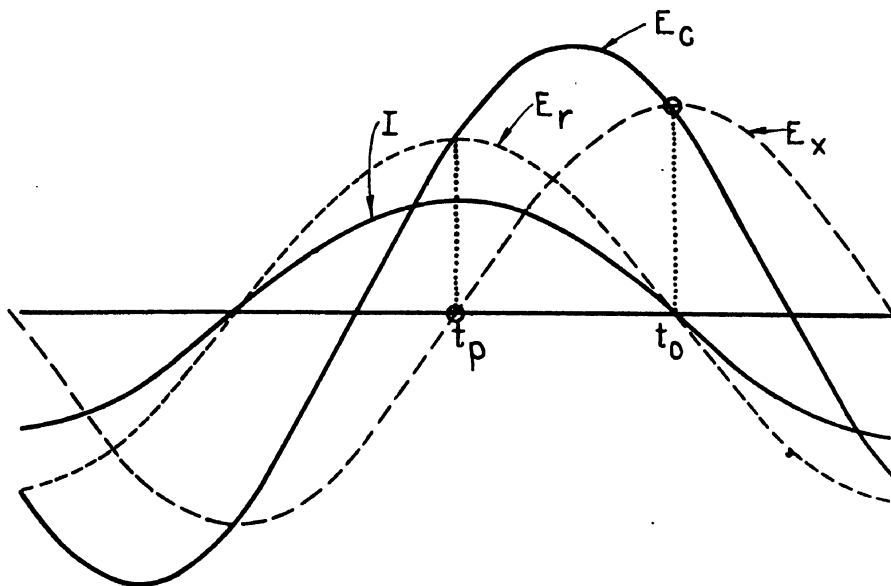


FIG. 19. The phase relations between a sinusoidal current through a conductivity cell and the associated electromotive forces. I , current through cell; E_r , E.M.F. impressed across resistance of column of electrolyte; E_x , E.M.F. impressed across surface films with abnormal concentration; E_o , total E.M.F. impressed on cell.

the hydrogen and chloride ions start to migrate in opposite directions to equalize the ionic concentrations at the face of the electrodes shown in figure 4. The rate at which the E.M.F. of the cell decreases to zero is inversely proportional to the sum of the ohmic resistances of the metallic discharge circuit connecting the platinum electrodes and the column of electrolyte between electrodes.

⁴ Actually when the switch opens and the cell starts to discharge through the resistance R_o of the E_o vibrator branch, the voltage recorded by the vibrator abruptly drops to a new value which is equal to $R_o/(R_o + R_c)$ times the value before the opening of S. This drop is so small for films 44 and 34 that it cannot be detected.

An examination of film 44 (figure 18) shows that after the opening of the switch S the E.M.F. of the cell decreases to zero along an exponential curve. The resistance and equivalent capacitance of the cell with 1 *N* hydrochloric acid as computed from the steady-state relations recorded on the film are 0.45 ohm and 4800 microfarads, respectively. Using these figures the computed value of the time-constant for the discharge curve works out to be 0.052 second, or 3.1 periods of the 60 cycles per second current. This computed value of the time-constant agrees (within the limits of the rather large scaling errors) with the value of the time-constant found by scaling the discharge curve itself.

In the case of film 34 (figure 15) the vibrator showing the E.M.F. of the cell was actuated by a vacuum tube voltage amplifier which presented a resistance in excess of 10,000 ohms to the discharge of the cell. For these conditions the computed value of the time-constant exceeds 48 seconds, and there should be no appreciable decrease in the E.M.F. of the cell during the time of the exposure. An examination of the film shows a slight fall in the E_c voltage immediately following the opening of S, after which the voltage of the cell undergoes no further apparent decrease. The initial change does not represent an actual decrease in the voltage across the cell, but is caused by the faulty performance of the voltage amplifier. The spontaneous discharge of the cell is therefore rather slow.

The above discussion of films 34, 35, 43, and 44 (figures 15, 16, 17, and 18) and figure 19 was predicated on a phase difference of 90° for a perfect capacitor and resistor in series, and a lag of the E_c curves somewhat less than 90° behind the I curves. The E_c curves in the above films actually lag the I curves slightly less than 90° , and tables 1, 2, and 3 show that θ_c is somewhat less than 90° . It was pointed out above that a conductivity cell has imperfect or "leaking" capacitance. In view of the above facts, of the effects of the asymmetry, rotation, and inertia of the ions and of the friction (viscosity), relaxation forces, and electrophoresis in the solvent on the rapidity of attainment of maximum or true mobility for a given potential difference, of the varying distribution of the current and capacitance at the electrode surfaces as shown by Snow (18), of the backward pull and migration of the ions under electrostatic forces arising from segregation, as when the current approaches zero value, of the inertia of the vibrator oscillograph in contrast with the cathode ray type, and other factors, such as the electrode-chemical reactions differentiating a conductivity cell from figure 19, the data probably agree with theory within the errors inherent in recording and scaling the wave forms on these films.

Mr. W. H. Goss has begun work on the study of the series capacitance by using a highly insulated vacuum tube potentiometer and cathode ray oscillograph to measure the E.M.F. changes over microseconds to hours

when cells are charged with direct currents from a primary cell or a capacitor below and above the polarization potential. The data show that plantinized electrodes require for discharge very short time periods to be measured with vibrator and cathode ray oscillographs. The results obtained to date harmonize with the present article.

VIII. DISCUSSION AND CONCLUSIONS

The oscillograms contained in this article have been obtained on two conductivity cells having large concentric cylinders of bright platinum spaced 1 mm. apart. Their dimensions lower the resistance of the column of electrolyte relative to the reactance of the *series* capacitance effects at the electrodes. This makes possible a better quantitative study of the relations. The conductivity of the solutions used was between 0.01 and 0.05 mho-cm.

It should be recognized that the scaling of the oscillograms for amplitudes and phase angles does not yield precise results. The errors of measurement (1 to 5 per cent) are large in comparison with those of our earlier precision A.C. bridge data on the cell. Our bridge measurements have shown that the simulating network comprising a resistor *in series* with a capacitor is only a first approximation to the actual cell, and that the second (and very precise) approximation is had by connecting a high resistance branch (leak) in parallel with the series capacitor (figure 1). The oscillograph method yields only a rough check of the first approximation, and can be expected to yield no data for a second approximation. With these limitations the following conclusions are drawn from the data.

1. Not only the steady-state relations but also the transient ones between the alternating current through a conductivity cell and the potential difference across its terminals have (within the limits of the large scaling errors) been shown to be identical with the relations between the current and the impressed E.M.F. which would be observed in a simulating network made by connecting an appropriate capacitor and a metallic resistor in series, provided the sum of the potential differences across the concentration layers does not exceed the E.M.F. of polarization of the solution.

2. The resistance of the column of electrolyte and the capacitive reactance of the equivalent series capacitor as computed by scaling the steady-state curves of current and impressed E.M.F. agree (within the limits discussed above) with the values computed from the transient curves.

3. Both the E.M.F. of ionic segregation (or the effect of the series capacitors C_1 and C_2 in the simulating network of figure 2) and the capacitance between electrodes and leads (the paralleling capacitors C_3 and C_4 of the network) cause the sinusoidal current through the cell to lead the sinusoidal E.M.F. impressed upon the cell. But for the cell and the 0.2 *N* sodium chloride solution used in this work, the angle of lead at

60 cycles per second due to the capacitance between electrodes (simulated by C_3 and C_4) is utterly insignificant, the computed angle of lead of the current being only 0.05 second of arc. On the other hand, at this same frequency the angle of lead due to the E.M.F. of ionic segregation (simulated by the series capacitors C_1 and C_2) is 58 degrees. Even at the audio frequency of 1000 cycles per second, the tangent of the angle of lead of the current due to the series capacitance effect is 44,000 times as great as that due to the parallel capacitance.

The capacitance of the simulating series capacitors C_1 and C_2 , as determined from the measurements on the oscillograms, is approximately 7000 microfarads, while the capacitance of the simulating parallel capacitors C_3 and C_4 , as computed from the dimensions of the cell, is approximately 1500 micromicrofarads. Because of the fact that the first of these capacitors is in series with the resistance of the column of electrolyte while the second is in parallel with the resistance, any direct comparison of the relative numerical values of the two capacitances is likely to be not only devoid of physical significance but also misleading. At a frequency of f cycles per second, the tangent of the angle of lead of the current due to a simulating capacitor of C_s farads in series with a resistor having R ohms resistance is $1/(2\pi f C_s R)$. On the other hand, the tangent of the angle of lead due to a capacitor of C_p farads in parallel with the same resistor of R ohms is $2\pi f C_p R$. From this it follows that to make the angle of lead infinitesimally small, a series capacitor C_s must be infinitely large, while a parallel capacitor C_p must be infinitesimally small.

4. The oscillograms show the departures from the sinusoidal shape of the current and electromotive force wave forms which occur when the E.M.F. of polarization of the cell is exceeded. Under an impressed E.M.F. greatly in excess of the polarization voltage, the current wave form again becomes approximately sinusoidal. This polarization peak-shift effect is associated with the greatly increased apparent capacitances and probably with electrode reactions other than ion segregation.

5. The oscillograms indicate that the value of the equivalent series capacitance of a given cell and solution is approximately independent of the measuring frequency at the two frequencies of 60 and 240 cycles, and is also independent of the value of the measuring E.M.F. and current provided the E.M.F. of polarization of the solution is not exceeded. With rise in the electrode potential E_e from 0.56 to 6.9 volts the apparent capacitance increases from 8700 to 46,700 microfarads, the transient terms decrease, and the peak value of the first current half-cycle approaches that for the steady state.

6. The preceding conclusions are consistent with the accurate data developed earlier by the use of precision bridges and sinusoidal currents at frequencies of 60 to 4000 cycles per second and extrapolation to infinite

frequency to obtain the true electrolytic conductances of solutions substantially free from the effects observed at high frequencies. It is suggested that in making the usual "solvent corrections" both the capacitance and conductance of the solvent be measured and used in interpretations of the conductance-capacitance properties of electrolytes.

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SURFACE VISCOSITY OF LONG-CHAIN ALCOHOL MONOLAYERS¹

LYMAN FOURT AND W. D. HARKINS

George Herbert Jones Chemistry Laboratory, University of Chicago, Chicago, Illinois

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INTRODUCTION

This work was undertaken with the purpose of providing a set of quantitative standards of surface viscosity, to clear the way for the more confident use of surface viscosity measurements in studies of molecular association and adsorption. Multivalent ions have very great effects on the viscosity and rigidity of fatty acid monolayers, and the interpretation that this is brought about by ionic bridges seems well supported. Films of macromolecules may show either great or very little shear resistance, and the adsorption of molecules beneath a film can sometimes be inferred from viscosity increases, as in the work of Langmuir, Schaefer, and Sobotka (4) with cholesterol and digitonin. The great desirability of more detailed knowledge of the relation of molecular structure to chemical reactivity and the special good fortune that the biological catalysts, the enzymes, are macromolecules makes it evident that a reliable method of interpreting viscosity in monolayers would be an important tool in the kit of the biophysicist. The underlying significance of surface viscosity may be seen from the fact that it is a measurable function related to the molecular binding energy within the plane of a monolayer, between molecules of specified orientation.

In order to simplify the problem as far as possible we have attempted to reduce the variables to two,—molecular length and orientation. As representatives of the two extreme types of molecular orientation, perpendicular and parallel to the surface, we have used the normal alcohols and the linear polymers of ω -hydroxydecanoic acid. The alcohols gave results of value for our purpose, but no viscosities large enough to measure could be obtained for the ω -hydroxydecanoic acid polymers. The alcohols have two special advantages as standards: (1) their force-area curves are simple, with two approximately straight lines, which indicates relative non-complexity of film structure; and (2) the effect of ions, etc., in the

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subphase should be less than on films with more reactive types of polar groups.

METHOD AND THEORY

The basic method is that used in the long series of studies of superficial viscosity dating back to Plateau (8) and in particular the work of Stables and Wilson in 1883 (10), Schütt in 1903 (9), Wilson and Ries in 1923 (13), Langmuir and Schaefer (3) in 1936 and 1937, and Myers and Harkins (6) in 1937. A circularly symmetrical body passes through the surface, and oscillates as a torsion pendulum about the vertical axis. The logarithmic decrement of the oscillations is proportional to the viscosity. Letting λ_{10} stand for the common logarithm of the ratio of successive amplitudes, and σ for the surface viscosity in c.g.s. units, we have

$$\sigma = \Delta\lambda_{10} \frac{2.3I}{2\pi P} \left(\frac{1}{a^2} - \frac{1}{b^2} \right) \quad (1)$$

where I is the moment of inertia, P is the period, a is the radius of the oscillating body, and b the radius of the bounding vessel. The value of $\Delta\lambda_{10}$ gives the change of decrement between the clean surface and that covered by the film, that is, applies a correction for the water resistance on the assumption that all of the change in resistance is caused by the film. This may include in the viscosity ascribed to the film an effect of accompanying water, but this effect, if any, would be a monotonic function of the true film viscosity. The period remains practically constant throughout the compression of any alcohol thus far encountered. The slight increase found can be attributed in part to the damping itself, as well as to increase in the rotational inertia because of accompanying water. Rigid films, however, contribute to the elasticity of the oscillating system and thus shorten P . The outer radius, b , was always large with respect to the inner radius, and was taken as 12.5 cm., the distance to the three nearest points on the bounding rectangle. A film balance of the horizontal thrust type (Langmuir-Adam) was used for simultaneous force-area control. The trough was 1.9 cm. deep.

Myers and Harkins (6) employed a sharp edged ring to reduce the water resistance, and a fairly large diameter, 10 cm., to increase the film effect. The ring was placed so that its sharp edge just touched the surface. These experiments have been continued, using rings of 3-in. and 1-in. diameter. The comparative data on different substances we obtained by using a disc 1 in. in diameter, the same diameter as that used by Langmuir and Schaefer (3). This disc, the end of a brass cylinder, was lowered until it just touched the surface. Phosphor bronze wires served for suspensions. The whole system was enclosed in a box to eliminate drafts. Two air jets were arranged to start or brake oscillation in either direction. The

parts in contact with the surface were always dipped in molten paraffin and allowed to drain freely while cooling, before each experiment.

Oberbeck in 1880 (7) and Fourt in 1937 (2) used an oscillating vane, instead of a circularly symmetrical system. Such a system has some distinct advantages in rigid films where slippage is a factor. From the damping of an oscillating vane of length l a surface viscosity may be computed

$$\sigma = \lambda_{10} \frac{4 \times 2.3I}{Pl^2} \quad (2)$$

on the assumption that the resistance arises from flow past the ends of the vane. Since this assumption is open to question, experimental comparisons with the ring and disc devices were made. The vane consisted of a microscope cover slip clamped between the halves of a slitted cylinder. It was cleaned with hot chromic acid and washed with water before each experiment, then put in place and lowered so that it just touched the surface.

The viscosity can also be computed from the torque required to maintain a uniform rotation. To do this we used the shaft of an electric clock motor for the upper suspension. The twist between the two ends of the torsion wire is measured by arranging two optical levers to throw spots of light from the moving suspension and from the rotating device onto the same scale. With the torsion constant, τ (dynes per radian), which is determined from oscillation trials, the torque can be obtained by timing the interval, t , between the passage of the two spots of light past a fixed mark. For true (Newtonian) viscosity, independent of the rate of shear, we have an equation in which the rate of rotation does not appear, although it must be constant. Here Δt is the change of interval caused by the film.

$$\sigma = \frac{\Delta t \tau}{4\pi} \left(\frac{1}{a^2} - \frac{1}{b^2} \right) \quad (3)$$

Anomalous viscosity or plasticity would cause a dependence on the rate of shear.

Although the experimental work with constant rotation is only preliminary, we have examined the theory because the interpretation of results with plastic films should be simpler for a method in which the rate of shear is constant, than for the oscillation methods in which the velocity is always changing. Moreover, of all the methods described here it seems the best adapted to the determination of the unique viscosity of the film without the effect of accompanying water. Hydrodynamic considerations indicate that absolute measurements of film viscosity could be obtained by using a device such as a hemisphere, to secure the condition that the

vertical velocity gradient in the underlying fluid should be zero in the plane of the surface. This condition could be approached, but the increase in non-film resistance requires greater sensitivity in measurement, and meniscus and centrifugal effects and the superposition of oscillation upon rotation may be expected to reduce the degree of realization of the theoretical conditions. However, the idea is adaptable, at least in theory, to interfacial measurements, by aligning the interface with the equatorial plane of the sphere.

The choice of the parameter for molecular orientation was dictated by experimental circumstances. With small damping as many as ten oscillations may be required for a single determination of the decrement, and with the high degree of damping encountered in the plastic films, a series of decrements was needed for the comparison at constant rate of shear. Hence an interval of several minutes was usually required for a single measurement. For the results to have significance with respect to molecular properties, it is desirable that the film structure remain the same throughout the measuring interval. The lower alcohols, however, showed a distinct tendency to disappear from the film, by collapse or, more probably, solution. That is, the force-area curve is dependent on the rate of solution, the rate of compression, and the elapsed time. A plot obtained by the rapid compression of a film of tetradecyl alcohol is paralleled by the curve obtained after an interval during which viscosities were measured. The area per molecule, computed on the basis that all of the alcohol spread remains on the surface, is less; the type of force-area relations is the same, however, and, what is most important, the intersections of the two straight limbs of the force-area curves are at the same pressure. For this reason the surface pressure is taken as the parameter to indicate the molecular state and resultant film structure. The area per molecule for the molecules actually present in the monolayer is presumably the same for these substances, at a given pressure, in spite of the apparent change with time. In the experiments the pressure was held constant by manual adjustment of the area. The imperfection of this type of control is a major source of random error. However, of the substances used, tetradecyl alcohol is the only one rapidly soluble or expanded at the temperatures used in these experiments, which ranged from 21° to 26°C.

In the preliminary work for the comparison of different devices, cetyl alcohol purchased from the Eastman Kodak Co. was used. For the comparison of the different alcohols we were privileged to use the preparations of Dr. Jane D. Meyer, which were kindly furnished us by Dr. E. E. Reid. Redistilled ligroin was used as a solvent in spreading these films. The ω -hydroxydecanoic acid polymers were kindly furnished by Drs. W. H. Carothers, E. O. Kraemer, and F. J. van Atta of the du Pont Experimental Station. The polymers were dissolved in redistilled benzene. All of the

alcohol films were spread on 0.01 *N* hydrochloric acid solution, made up in redistilled water.

RESULTS

All the alcohols from tetradecyl to heptadecyl showed viscosity relations of the same general type. The kink point of the force-area curve is likewise a singular point in viscosity. At all lower pressures the films behave as Newtonian fluids. At all higher pressures the films exhibit anomalous viscosity, that is, the apparent viscosity increases with decreasing rate of shear. Harkins and Myers (6) referred to this as plasticity, as did Wilson and Ries (13) for their adsorbed films. However, we use the term

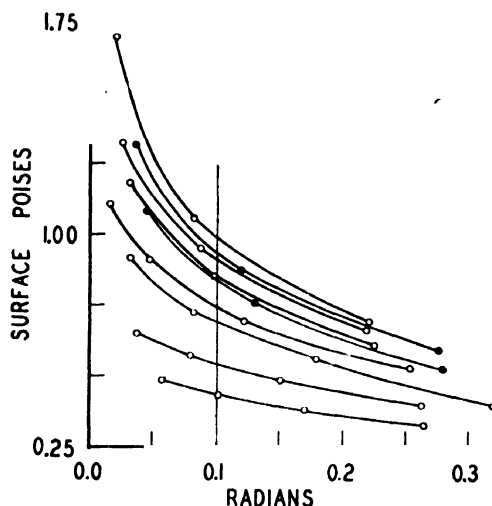


FIG. 1. Representative family of curves to show the dependence of viscosity on the rate of shear above the kink point pressure. Ordinate, apparent surface viscosity; abscissa, mean amplitude. The open circle curves are all at successively higher pressures and viscosities up to the viscosity maximum. The solid circles lie on curves for still higher pressures but decreasing viscosities.

“plastic” merely as a convenient expression for anomalous viscosity, because our methods do not give us any measure of a yield point. Moreover, sensitive tests for rigidity, by means of the oscillating vane, observation of talc mobilities, and the behavior of floating strips of paper (Langmuir and Schaefer (3)) fail to give any evidence of rigidity.

The variation of apparent viscosity with rate of shear or amplitude, which is encountered above the kink point, has been treated by an empirical method designed to make the successive values in a given experiment comparable. To do this, the logarithmic decrement or the apparent viscosity was plotted against the sum of the amplitudes used in its computation. An example of the resulting families of curves is shown in figure 1. These

curves do not cross each other, except for occasional irregularities, which shows that "greater than or less than" comparisons are justified. The values for the plastic films are those taken at a mean amplitude of 0.1 radian, but the greatest viscosities recorded in the plastic region were several-fold larger; the smallest was about half as large.

The transition at the kink point is very nearly free from hysteresis. Points taken by expanding a compressed film fall on the same curve, to the accuracy of this work, as those obtained by successive compressions. This type of experiment was tried with tetra-, hexa-, and hepta-decyl alcohols. It is not impossible that a more nearly instantaneous method of measurement might reveal a hysteresis or sluggishness obscured by the time required for a series of oscillations. In the steep part of the curve a second series of oscillations at a given pressure usually gives a higher apparent viscosity. With two films of tetradecyl alcohol, low values of the viscosity were obtained above the kink point. Although this may

TABLE 1
Dimensions of oscillation devices

TYPE	RADIUS OR LENGTH	MOMENT OF INERTIA	PERIOD IN CLEAN SURFACE	λ_{10} IN CLEAN SURFACE	APPARATUS CONSTANT $\div P$
	<i>cm.</i>	<i>g. cm.²</i>	<i>sec.</i>		
Ring.	5.00	2520	73.40	0.042	0.426
			10.88	0.0082	2.87
	3.91	695	33.68	0.034	0.476
Disc.	1.26	141	17.69	0.0051	1.88
	1.26	127	16.88	0.0075	1.70
Vane.	3.00	202	17.80	0.0030	11.6
	6.00	177	17.91	0.051	2.52

correspond to a metastable state, like a condition of undercooling or supersaturation, a comparatively large number of repeated experiments with this substance have not enabled us to specify the conditions under which this behavior may be observed.

Except for octadecyl alcohol, the viscosity is Newtonian until well into the steep part of the transition curve. It is not a matter of the magnitude of the observed value of λ_{10} , since experiments with devices in which λ_{10} is large and the factor small agree with those used in the comparative work. Octadecyl alcohol differed in showing a slight plasticity below the kink point. This effect is small compared with the difference between check experiments on different films, but could be seen clearly in an individual experiment. Octadecyl alcohol has the further peculiarity that the curves which show the viscosity as a function of the amplitude, although they rise with decreasing amplitude, are nearly straight, in contrast to the considerable curvature found with the other alcohols.

The hexadecyl alcohol samples from the two sources (Eastman, and Meyer and Reid) gave nearly the same numerical values below the kink point, but above the kink point the Eastman sample showed values about half as large, though with a curve of similar shape. For a comparison of the different oscillation methods we may confine our attention to the values below the kink point. Table 1 shows the dimensions of the different systems used, the approximate value of λ_{10} for the clean surface, and the factor "apparatus constant $\div P$ " by which the change in λ_{10} is multiplied to obtain σ .

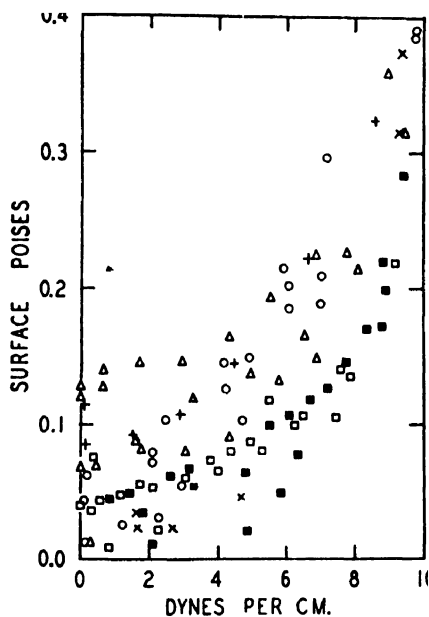


FIG. 2

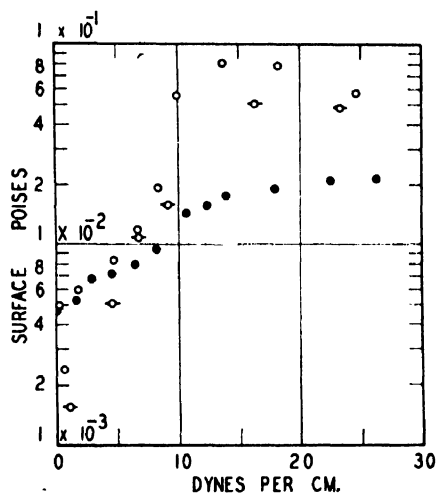


FIG. 3

FIG. 2. Surface viscosity of hexadecyl alcohol below the kink point, as measured by different devices. Ordinate, surface viscosity; abscissa, surface pressure. O, 10-cm. ring; Δ , 3-in. ring; \square , 1-in. ring; \blacksquare , 1-in. disc; +, 6-cm. vane; \times , 3-cm. vane.

FIG. 3. Surface viscosity of hexadecyl alcohol from constant rotation measurements. Ordinate, logarithm of viscosity; abscissa, surface pressure.

Figure 2 presents the results obtained with the different methods. Check experiments with each device show a range of values comparable to the difference between different devices; there is just a suggestion of a trend in that the largest values are obtained with the rings of largest diameter, and the smallest with those of smallest diameter. This may involve the approximation introduced by taking the half-width of the rectangular tray as an outer circular boundary. Most of the points with the 10-cm. ring were computed from the experiments of Myers (6). The values obtained with vanes 3 and 6 cm. long fall among the others. Above

the kink point all of the devices give values similar in magnitude and in variation with pressure, the agreement being of the same order as that exhibited below the kink.

Figure 3 shows some preliminary results obtained for hexadecyl alcohol from the rotation of the 10-cm. and 3-in. rings, some with stopwatch timing and some by an automatic timing system. This apparatus could be adapted to automatic recording. Below the kink point these values are of the same order as those obtained by the oscillation methods, but are tenfold smaller above. The comparatively large angular velocity, 0.387 radian per second, compared with 0.0237, the average speed in oscillation at 0.1 radian, with $P = 16.88$ sec. is in the direction to account for this difference. The points were taken too far apart and the timing interval available was too coarse to do more than indicate the potentialities of the method.

The choice of apparatus for the work with different substances was somewhat arbitrary. The lower limit of viscosity measurable by any of the oscillation devices is about the same, as may be seen from the constancy of the product of "apparatus constant $\div P$ " times unity in the place of the last significant figure of the clean surface λ_{10} (given in table 1). For this reason the work has been confined to a straightforward application of methods, such as would be desirable for exploratory experiments and routine testing. By an increased expenditure of time and a statistical analysis of the results any of these devices could be used to measure viscosities as low as 0.0002 surface poise.

The viscosities of the normal alcohols from C_{14} to C_{18} inclusive are shown in figure 4. The portions above and below the kink point are plotted on different arithmetic scales of viscosity, and the very high pressures are shown on a contracted scale. With increasing chain length, the kink points lie at increasingly higher pressures. The viscosities at low pressures are larger, the longer the chain. Below the kink point the viscosity of each alcohol increases with increasing pressure, and the more rapidly as this singular point is approached. The transition is more abrupt for the shorter chain.

Above the kink point the apparent viscosity of each alcohol tends to increase for a range of pressures, and finally, as collapse is approached, to fall off again. The scattering of values between different experiments on the same substance is more pronounced above than below the kink. Nevertheless, the trend of viscosity with chain length is clear: the longer the chain, the less the apparent viscosity. With respect to what we may call the degree of plasticity, the rate of change of apparent viscosity with amplitude, the trend is also reversed, octadecyl alcohol being the only one plastic below the kink point, and the least so above. No great degree of difference could be seen in the plasticity of the other alcohols, however.

The whole range of the viscosities of all of the alcohols can be shown on a single figure by plotting the viscosities on a logarithmic scale (figure 5). The range of values—nearly 10,000-fold—and the magnitude of the transition at the kink point is emphasized. Below the kink point the logarithm of the viscosity increases somewhat more rapidly than linearly with pressure.

The insert in figure 5 presents the mean values taken from the logarithmic plot, plotted against pressure expressed as fraction of the kink point

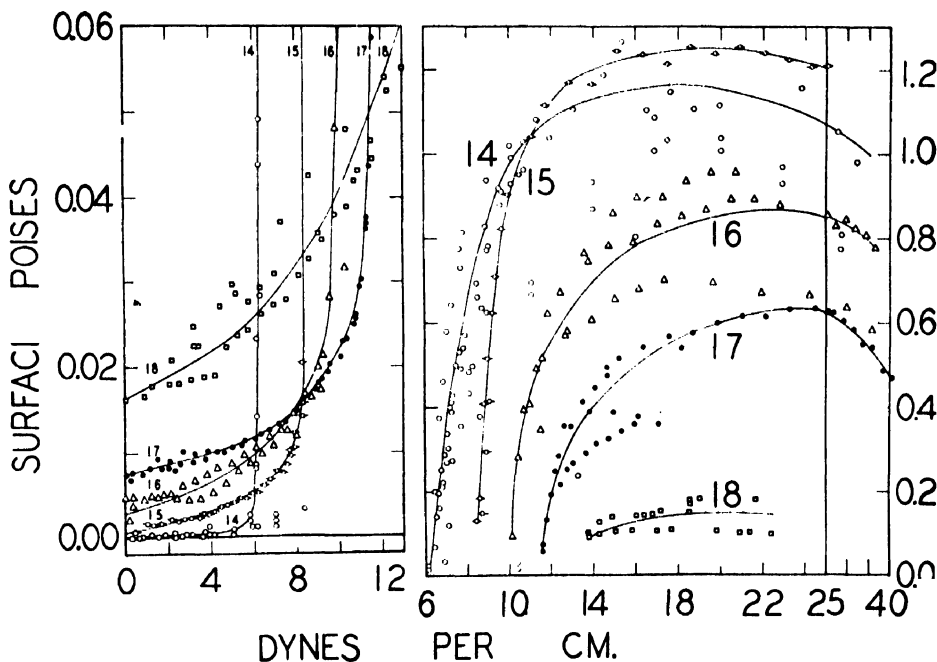


FIG. 4. Surface viscosities of the normal alcohols from C_{14} to C_{18} . Left-hand part, below the kink point; right-hand part, above the kink point, showing apparent viscosities at 0.1 radian mean amplitude. Ordinates, surface viscosity; abscissae, surface pressure. Pressures above 25 dynes per centimeter are shown on a reduced scale. On the low pressure side, the bottom of the plot represents -0.002 surface poise, to show that "negative viscosities" are not significant.

pressure. This corresponding states graph facilitates comparison by omitting the crossing over with the reversal of order at the kink point. From this figure it is seen that below the kink point the viscosity increases with increasing chain length. Above the kink point pentadecyl alcohol is shown out of order; the fields of points represented by these median lines are so overlapping, though, for tetra-, penta-, and hexa-decyl alcohols, that only the general trend toward lower apparent viscosity with longer chain is significant.

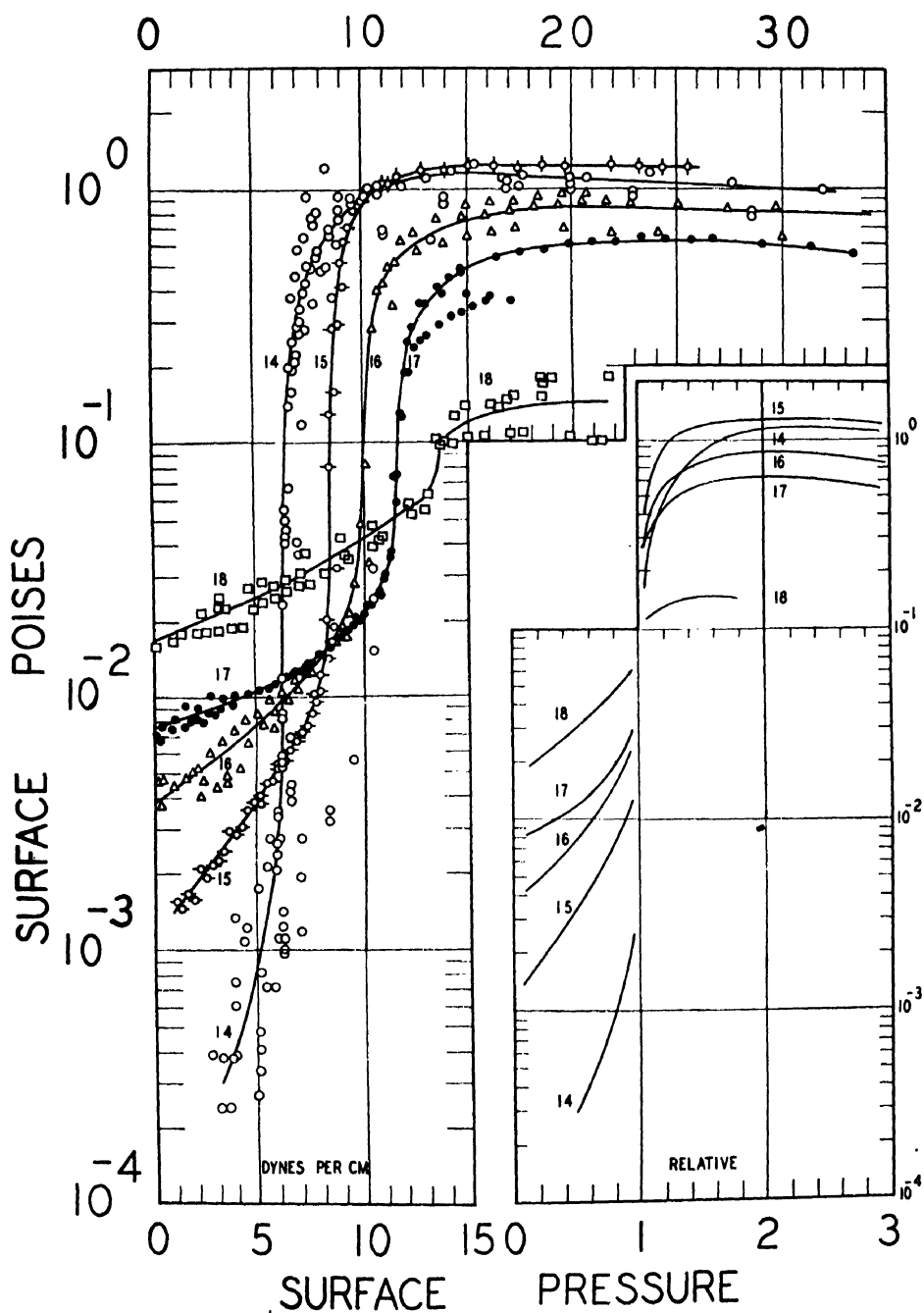


FIG. 5. Surface viscosity of the normal alcohols from C_{14} to C_{18} . Ordinate, logarithm of surface viscosity; abscissa, surface pressure. In the insert the surface pressure scale is in multiples of the mean kink point pressure.

Neither with respect to kink point pressures nor with respect to viscosities is there any alternation evident between odd and even numbers of carbon atoms in this series. This parallels the absence of alternation of melting point found by Meyer and Reid (5).

The mean values of the kink points for the different alcohols are given in table 2, which also shows the values reported by Adam and Dyer (1). The mean values given are the midpoints of the transition curves of viscosity shown in figure 5 and are accurate within 0.5 dyne. Within this limit they agree with the kink points determined from force-area measurements on the same samples in this laboratory.

The force-area curves of tetradecyl alcohol show a curved portion below 3 dynes pressure. This corresponds to the expanded type of film, which has too low a viscosity to measure, as may be seen in figure 5. All the other alcohols had measurable viscosities even at 0.1 dyne pressure, and

TABLE 2
Transition pressures of the normal alcohols

ALCOHOL	PRESSURES, IN DYNES PER CENTIMETER	
	This work	Adam and Dyer
C ₁₄	6.2	7.2
C ₁₅	8.5	
C ₁₆	10.0	9.2
C ₁₇	11.6	
C ₁₈	13.4	11.0
C ₂₀		13.5

these viscosities lie fairly well on the same smooth curve as those at higher pressures. At quite large areas, though with the film at practically zero pressure, one frequently observes a very small "negative viscosity," that is, a damping less than that of the original clean surface. This is, however, never much larger than the random fluctuation of the damping caused by the clean surface, and thus is hardly significant, as the arithmetic plot of figure 4 shows. This anomaly is less marked with the disc than with any of the rings. The C₁₂ alcohol is quite soluble and has an entirely expanded force-area curve at room temperature. It showed no measurable viscosity.

Likewise, we were unable to measure any viscosity for ω -hydroxydecanoic acid polymers of molecular weights 780 and 16,900, spread on 0.01 *N* hydrochloric acid or sodium hydroxide, or on sodium hydroxide to which a calcium salt had been added. Only on collapse and compression to a visible scum could a change in damping be obtained. Collapse occurs at comparatively low pressures, however (ca. 3 dynes per centimeter).

DISCUSSION

The relation of viscosity and of compressibility to the kink point is significantly different. To a close approximation, the two limbs of the force-area curve of the alcohols are straight lines, intersecting sharply, implying a discontinuity in compressibility. By contrast the change in viscosity, although large in magnitude and extreme in quality (reversal of relationship to molecular length), is continuous and spreads out on either side of the main transition.

Recent detailed studies of the region of the kink point for these substances, made in this laboratory by Dr. G. C. Nutting, show a previously unnoticed phenomenon; a slight increase in compressibility and an increased tendency of the pressure to fall off with time become evident just below the kink. This effect is found in a pressure range of about 0.5 dyne above and below the "kink" determined by the extrapolated curves.

TABLE 3
Computed bulk viscosities of the normal alcohols

ALCOHOL	FILM THICKNESS AT		MEAN SURFACE VISCOSITY		COMPUTED BULK VISCOSITY	
	21.6 Å. ² per molecule	19.0 Å. ² per molecule	Smallest	Maximum	Smallest	Maximum
	Å.	Å.	surface poises		poises	
C ₁₄	19.9	22.7	0.0003	1.15	1.5×10^2	5.1×10^6
C ₁₅	21.2	24.2	0.0015	1.25	0.7×10^4	5.2×10^6
C ₁₆	22.5	25.7	0.0040	0.85	1.8×10^4	3.3×10^6
C ₁₇	23.8	27.2	0.0075	0.62	3.2×10^4	2.3×10^6
C ₁₈	25.1	28.7	0.0165	0.18	6.6×10^4	0.6×10^6

Adam's distinction between close-packed heads and close-packed chains was suggested by the force-area relations. Without making such a detailed picture as is implied by those phrases, we may speak of low and high pressure condensed films, and of a transition range.

The state of aggregation of the molecules in the structure predominating above the kink point must be left unsettled. Plasticity is a more convenient expression than anomalous viscosity, but it must be emphasized that a solid, in addition to phenomena of non-Newtonian deformation or flow, should show a yield point and especially the property of shear elasticity.

There is no necessity for an explanation of the decline of the apparent viscosity at the higher pressures in terms of film structure. For what they interpreted as a maximum strength phenomenon in monolayers, Talmud, Suchowolskaja, and Lubman (11) have postulated lessened inter-twining of the more perfectly oriented chains and consequent more ready

slippage under shearing stress. The viscosity maximum observed in the present experiments could also arise from an instability of the film with the approach of collapse. Under shearing stress molecules could yield by escaping from the plane of the film, the more readily the higher the pressure. These experiments offer no basis for choice.

A formal calculation of bulk viscosity may be made by dividing the surface viscosity by the vertical thickness of the films. If we take 21.6 \AA^2 as the area per molecule at 0.1 dyne pressure for all the compounds, and 19 \AA^2 as the area at the pressure of maximum viscosity, and use 0.82 as a round number for the density, the mean thickness of the monolayer can be computed for each alcohol. The corresponding ordinary viscosities are given in table 3.

When we consider that the viscosity of water at room temperature is 1×10^{-2} poises we see that the smallest values measured are from 10^4 to 10^6 times that, and that the maximum values are some 10^8 -fold larger than for water. These might be regarded as excessively high values because of the participation of accompanying water, not taken into account in computing the film thickness. However, there is no reason apparent why more water should accompany one alcohol than another. This supports the idea that the differences found are really in the plane of the monolayer. Trouton and Andrews (12) found the viscosity of shoemaker's wax to be 5×10^6 , of pitch around 10^{10} , and of soda glass 10^{13} poises. This would tend to show that there is nothing intrinsically unreasonable in the magnitudes of the maximum values encountered in this work.

SUMMARY

Methods based on the damping of oscillating rings, discs, and vanes by a surface film give values of the surface viscosity which agree well enough to indicate the usefulness of such methods. A continuous rotation device, although not yet refined to the same degree of usefulness, gives similar values. Theory indicates that such a device would possess advantages for use with plastic films, and that it could be adapted to give absolute values of surface and interfacial film viscosities, free from subphase effects.

The viscosity of expanded films of the normal alcohols is too low to measure by these means. Measurements were obtained on condensed films of the five alcohols from C_{14} to C_{18} inclusive. The low pressure linear part of the compression curve corresponds to low values of the surface viscosity, increasing more and more rapidly with increasing pressure. For this portion the longer the chain, the higher the viscosity. The high pressure linear part of the compression curve corresponds to high apparent viscosities, which are greater for lower rates of shear. These values, compared at a single average rate of shear, rise to a maximum as the pressure increases, then fall off with the approach of film collapse. Of the alcohols

examined, only octadecyl alcohol shows non-Newtonian viscosity below the kink point. The singular point or, as recent findings show, region of the force-area curves corresponds to the transition in viscosity.

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THE VISCOSITY OF DILUTE SOLUTIONS OF LONG-CHAIN MOLECULES. I^{1,2}

MAURICE L. HUGGINS

Kodak Research Laboratories, Rochester, New York

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INTRODUCTION

This paper is a report of an attempt to develop a satisfactory theory, heretofore lacking, of the viscosity of dilute solutions of long-chain compounds.

For solutions or suspensions of *incompressible, spherical* particles which are *large* in comparison with the molecules of the solvent, Einstein (3, 4) has derived the relationship

$$\eta_{sp} = \frac{5}{2} \frac{v}{\bar{V}} \quad (1)$$

For solutions or suspensions of particles consisting of spheres rigidly held together to form a rod-like molecule (the distance between sphere centers being twice the sphere diameter), Kuhn (15, 16) deduced the equation

$$\eta_{sp} = \frac{v}{\bar{V}} \left(\frac{5}{2} + \frac{f_1^2}{16} \right) \quad (2)$$

In the derivation he assumed that the Brownian motion is large in comparison with the velocity gradient in the solution.

For ellipsoidal particles Eisenschitz (5, 6) derived the equation

$$\eta_{sp} = \frac{v}{\bar{V}} \left(\frac{1.15f_2}{\pi \ln 2f_2} \right) \quad (3)$$

neglecting the Brownian motion, and

$$\eta_{sp} = \frac{v}{\bar{V}} \left(\frac{f_2^2}{15 \ln 2f_2 - \frac{45}{2}} \right) \quad (4)$$

for very long particles, with a large Brownian motion effect.

¹ Presented at the Fifteenth Colloid Symposium, held at Cambridge, Massachusetts, June 9-11, 1938. A preliminary report of this work was presented at the Ninety-fourth Meeting of the American Chemical Society, held at Rochester, New York, September, 1937.

² Contribution No. 647 from the Kodak Research Laboratories.

In these equations,

$$\eta_{sp} = \frac{\eta}{\eta_0} - 1$$

is the fractional increase in viscosity of the solution over that of the pure solvent, v/V is the volume of solute per unit volume of solution, f_1 is the ratio of the length of the rod-like molecule to the diameter of the spheres of which it is composed, and f_2 is the axial ratio of the ellipsoid.

Empirically Staudinger (26, 27, 28) showed that, for very dilute solutions of several types of long-chain compounds, the specific viscosity divided by the concentration in submoles ("Grundmole") per liter is approximately

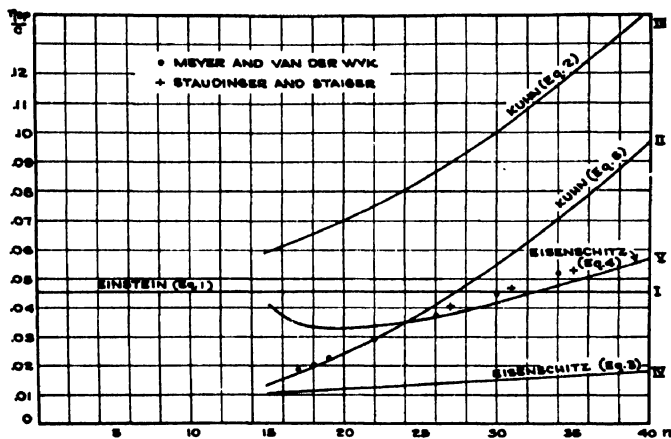


FIG. 1. Experimental and previous theoretical values of η_{sp}/c for dilute solutions of paraffins in carbon tetrachloride at 20°C.

proportional to the number of *submolecules* ("Grundmoleküle", e.g., CH_2 groups in a paraffin chain) in the chain:

$$\frac{\eta_{sp}}{c} = k_s n \quad (5)$$

This empirical relationship has been much used by Staudinger and others in deducing approximate average molecular weights of high polymers.

The experimental viscosity data of Meyer and van der Wyk (22) and of Staudinger and Staiger (28) for solutions of normal paraffins are compared with the theoretical values calculated from equations 1, 2, 3, and 4 in figure 1. Since, in the writer's opinion, the inclusion of an Einstein incompressibility term $\left(\frac{5 \cdot v}{2 \bar{V}}\right)$ in equation 2 for rod-like molecules is very questionable, a curve representing the equation

$$\eta_{sp} = \frac{v}{\bar{V}} \left(\frac{f_1^2}{16} \right) \quad (6)$$

is also included in the figure.

It is evident that none of the theoretical curves is satisfactory. The experimental points lie approximately on a straight line, but (from Meyer and van der Wyk's data at least) not one that passes through the origin.

Aside from this comparison, there is considerable other evidence favoring the supposition that long-chain molecules, such as the paraffins, are very much kinked in solution, rather than straight. The rigidity of such kinked molecules is more questionable, although there is considerable evidence (10, 11, 12, 13, 14, 23, 24, 25; cf., however, 1) for the existence of potential energy humps of the order of magnitude of 3000 cal. (i.e., about 5 times RT) per mole tending to prevent rotation about each single bond in a paraffin chain. If so, intermolecular collisions will only very rarely have sufficient energy to produce rotation over these energy humps, but rotation through a few degrees will take place much more readily.

In view of the foregoing, a theoretical calculation of the viscosities of dilute solutions of rigid, randomly kinked chain molecules has been made,

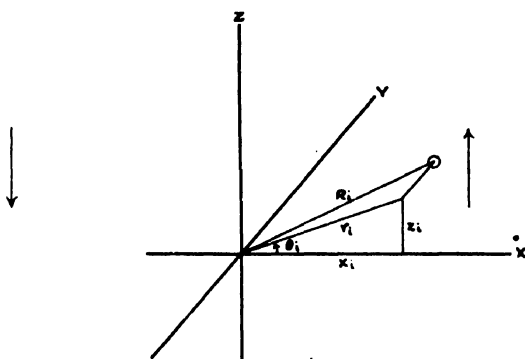


FIG. 2. Illustrating the orientation of reference axes, etc.

with some progress in extending the results to non-rigid, kinked chain molecules. Only an outline of the methods and results will be presented here; the details will be given in a later paper.

DERIVATION OF A GENERAL EQUATION FOR RIGID MOLECULES

We first consider a rigid molecule in dilute solution and, following an elaboration and extension of Kuhn's procedure (15, 16, 17), calculate the relation between the work done on this molecule by the solution as a function of the velocity gradient of the solution, the viscosity of the solution, and the coördinates of the atoms in the molecule.

The origin is taken at the center of moments of the molecule, with the axes so oriented that the surrounding liquid moves in the Z direction with a velocity, qx , which is proportional to x . The atoms are numbered 1, 2, 3 . . . i . . . n and their coördinates designated as x_i , y_i , z_i (see figure 2).

Because of the velocity gradient in the liquid, the molecules rotate about the Y -axis. We represent the length of the vector from the origin to the projection of the atom i onto the XZ plane by r_i and the angle measured counterclockwise from the X -axis to this vector by Θ_i .

The work expended on atom i in unit time is deduced to be

$$\epsilon_i = 6\pi\eta q^2 a_i \frac{[z_i^2(\Sigma a_i x_i^2)^2 + x_i^2(\Sigma a_i z_i^2)^2]}{(\Sigma a_i r_i^2)^2} \quad (7)$$

The work expended on all n atoms, if they all have the same radius a , is

$$\epsilon = 6\pi\eta q^2 a F_{zz} \quad (8)$$

where

$$F_{zz} = \frac{\Sigma x_i^2 \cdot \Sigma z_i^2}{\Sigma r_i^2} = \frac{\Sigma r_i^2 \cos^2 \Theta_i \cdot \Sigma r_i^2 \sin^2 \Theta_i}{\Sigma r_i^2} \quad (9)$$

From this is derived the relationship:

$$\frac{\eta_{sp}}{c} = \frac{6\pi N a \overline{F_{zz}}}{1000n \left(1 - \frac{6\pi N a \overline{F_{zz}}}{1000n} c\right)} \quad (10)$$

in which N is Avogadro's number and $\overline{F_{zz}}$ is the average of F_{zz} over all orientations.

It can be shown that, if

$$\frac{6\pi\eta a q (\Sigma r_i^2 \cos^2 \Theta'_i - \Sigma r_i^2 \sin^2 \Theta'_i)}{kT}$$

is small compared to unity (k being the Boltzmann constant and T the absolute temperature), then

$$\begin{aligned} \overline{F_{zz}} = \frac{\Sigma \overline{R_i^2}}{12} + \frac{1}{3} \left[\frac{\Sigma R_i^2 \sin^2 \Theta'_i \cdot \Sigma R_i^2 \cos^2 \Theta'_i}{\Sigma R_i^2} \right]_{\text{ave.}} \\ - \frac{1}{3} \left[\frac{(\Sigma R_i^2 \sin \Theta'_i \cos \Theta'_i)^2}{\Sigma R_i^2} \right]_{\text{ave.}} \end{aligned} \quad (11)$$

The angles Θ_i are constants, being measured relative to an arbitrary set of X - and Z -axes rotating with the molecule.

APPLICATION TO RIGID CHAIN MOLECULES

For linear rod-like molecules equation 11 reduces to

$$\overline{F_{zz}} = \frac{l^2(n^2 - n)}{144} \quad (12)$$

With large n and small concentrations, from equation 10,

$$\frac{\eta_{sp}}{c} \approx \frac{\pi N a l^2 n^2}{24000} \quad (13)$$

We next consider a rigid, randomly kinked, centrosymmetric chain molecule. For the average value of R_i^2 we make use of a relationship, derived by Eyring (7),

$$\overline{R_i^2} = l^2 B i \quad (14)$$

where

$$B = 1 + 2 \left(\frac{i-1}{i} \right) \xi + 2 \left(\frac{i-2}{i} \right) \xi^2 + 2 \left(\frac{i-3}{i} \right) \xi^3 + \dots + 2 \xi^{i-1} \quad (15)$$

$$\xi = \cos \alpha \quad (16)$$

and α is the supplement of the angle included between adjacent bonds (see figure 3).

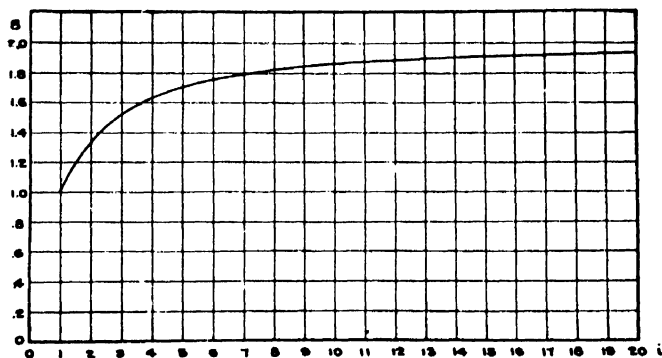


FIG. 3

By an extension of Kuhn's (18) statistical methods, it is possible to show that the average of the square of the distance of the i^{th} atom of the chain molecule from the straight line joining the origin (at the center of the molecule) to the end (m^{th}) atom is

$$\overline{S_i^2} = \frac{2}{3} B l^2 \left(i - \frac{i^2}{m} \right) \quad (17)$$

Also,

$$\overline{R_i^2 \sin^2 \Theta'_i} = \frac{3}{4} \overline{S_i^2} \quad (18)$$

$$\overline{R_i^2 \cos^2 \Theta'_i} = \overline{R_i^2} - \frac{3}{4} \overline{S_i^2} \quad (19)$$

Making the approximations

$$\left[\frac{\Sigma R_i^2 \sin^2 \Theta'_i \cdot \Sigma R_i^2 \cos^2 \Theta'_i}{\Sigma R_i^2} \right]_{\text{ave.}} \approx \frac{\overline{\Sigma R_i^2 \sin^2 \Theta_i} \cdot \overline{\Sigma R_i^2 \cos^2 \Theta_i}}{\overline{\Sigma R_i^2}} \quad (20)$$

$$\left[\frac{(\Sigma R_i^2 \sin \Theta'_i \cos \Theta'_i)^2}{\Sigma R_i^2} \right]_{\text{ave.}} \approx 0 \quad (21)$$

and performing the summations, we obtain

$$\overline{F_{zz}} = 0.0324\beta B_\infty l^2 a(n^2 - 2n + 1) \quad (22)$$

$$B_\infty = \frac{1 + \xi}{1 - \xi} \quad (23)$$

in which β is a complicated function of n which approaches unity as n increases (see figure 4).

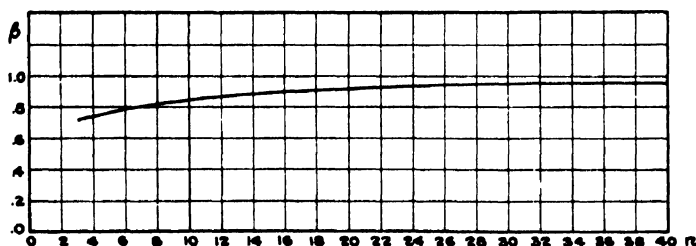


FIG. 4

By a complicated procedure, involving an analogy with a rod-like molecule bent in the middle, with all angles of bending equally probable, a factor of 4/5 has been calculated for the conversion of $\overline{F_{zz}}$ for randomly kinked *centrosymmetric* molecules to $\overline{F_{zz}}$ for otherwise similar molecules which do not necessarily have centers of symmetry. For this more general case, then,

$$\overline{F_{zz}} = 0.0259\beta B_\infty l^2 a(n^2 - 2n + 1) \quad (24)$$

$$\frac{\eta_{sp}}{c} = \frac{4.84 \times 10^{-4} N\beta B_\infty l^2 a(n - 2)}{1 - 4.84 \times 10^{-4} N\beta B_\infty l^2 a(n - 2)c} \quad (25)$$

For large values of n and small values of c equation 25 reduces to

$$\frac{\eta_{sp}}{c} = 4.84 \times 10^{-4} N\beta B_\infty l^2 a n \quad (26)$$

We thus have a theoretical derivation of Staudinger's empirical viscosity law (26).

EXTENSION TO NON-RIGID CHAIN MOLECULES

An attempt has been made to determine the effect of introducing flexibility (resulting from free or restricted rotation about the bonds in the chain) into the molecular model. The problem is a complicated one, which will be dealt with in detail at another time. For the present a few comments will suffice.

In general, the viscosities should be nearly the same for flexible long-chain, kinked molecules as if they were rigid. The solvent exerts a stretching force for Θ , between 0 and $\pi/2$ and between π and $3\pi/2$ and a compression force during the rest of the rotation. Tending to counteract this is the entropy change, which can be calculated approximately (2, 8, 9, 18, 19, 21). As a net result it can be shown that the η_{sp}/c values, as calculated

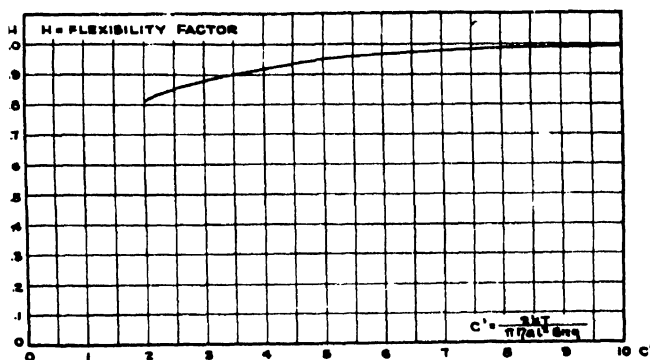


FIG. 5.

for a rigid molecule, should be multiplied by a "flexibility factor," H , which varies with

$$C' = \frac{2kT}{\pi \eta a^2 B n q} \quad (27)$$

approximately as indicated in figure 5.

In addition, a small constant term should be added to η_{sp}/c to allow for rotation of units other than at the ends of the chain and a term of the form $const./n$ to cover rotation of the atoms and groups near the ends.

COMPARISON WITH EXPERIMENTAL DATA

The best experimental data now available for testing these theoretical results are for solutions of the paraffins (22, 28). We use equation 25 for rigid, randomly kinked molecules, rough calculations indicating that the corrections for flexibility would not make much difference in the result.

In agreement with x-ray and electron diffraction data we take

$$l = 1.54 \times 10^{-8} \text{ cm.} \quad (28)$$

and assume tetrahedral bond angles, hence

$$B_{\infty} = 2 \quad (29)$$

The effective radius, a , must be of the order of magnitude of 10^{-8} cm. Certain qualitative considerations suggest that it should approximately equal the radius of the sphere having the same surface area as the surface, per unit segment, of the molecule, considered as cylindrical. If this is assumed we calculate, from the density of liquid paraffins,

$$a = 1.28 \times 10^{-8} \text{ cm.} \quad (30)$$

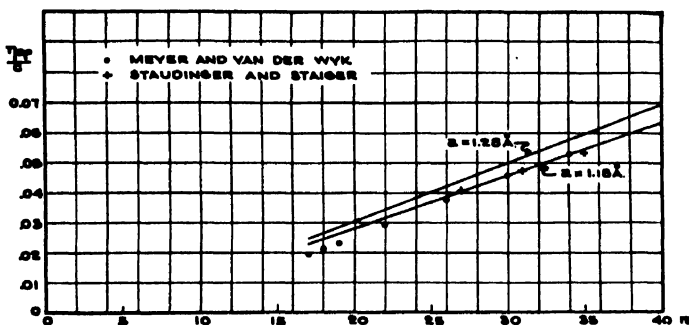


FIG. 6. Experimental and theoretical values (from equation 25) of η_{sp}/c for dilute solutions of paraffins in carbon tetrachloride at 20°C.

Substituting these values for l , B_{∞} , and a in equation 25 and reading β from figure 4, the values used in plotting the upper curve of figure 6 are obtained. If the slightly lower value, $a = 1.18 \times 10^{-8}$ cm., is used, the lower curve is obtained. The agreement is very satisfying, considering the method of estimating a and other approximations used in the derivation. The slope of the theoretical curve lies between that of the curve through Meyer and van der Wyk's values and that of the curve through Staudinger and Staiger's results.

Comparisons with experimental data for other series of compounds will be made at another time.

THE MCBAIN EXPERIMENTS

McBain and McBain (20) compared the velocities of fall through sucrose solutions of quartz fibers and quartz spheres of the same weight and volume, showing that the difference in frictional resistance to movement of these particles is by no means sufficient to account for the observed high

viscosities of dilute solutions of long-chain compounds. They conclude, therefore, "that the chief factor is structural viscosity due to entanglement and local adherence of molecules and particles, effectively immobilizing a disproportionate amount of the solvent in comparison with the amount of the colloid itself."

It should be pointed out that the McBain experiments bear little or no relation to the problem, since in their experiments the velocity of one side of the particle relative to the surrounding liquid is the same as that of the other side. In any viscosity determination a velocity gradient is set up. As is shown in this paper (and has been shown previously by others), it follows from classical hydrodynamics that *because of this velocity gradient* frictional work is done on non-spherical particles by the liquid. This effect must exist, and the evidence presented here shows that its magnitude is such as to account practically quantitatively for the experimental data, at least for dilute solutions of paraffins.

SUMMARY

By an extension of Kuhn's hydrodynamical treatment a theoretical equation has been derived relating the specific viscosity of a solution to the coördinates and dimensions of the atoms in the solute molecules. Applied to rod-like molecules this equation leads to proportionality (with n large) between η_{sp}/c and n^2 . Applied to randomly kinked chain molecules, it leads to proportionality between η_{sp}/c and n , the Staudinger relationship.

Theoretical expressions have been obtained for the proportionality constant and also for the deviations for small values of n . Using a reasonable value for the "effective radius" of the CH_2 group, without any arbitrary constants whatever, the experimental data for solutions of paraffins are quantitatively accounted for.

In conclusion, it is a pleasure to give acknowledgment to Miss Dorothy Owen, who performed a large part of the necessary calculations during the preparation of this paper.

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THE VISCOSITY OF CELLULOSE IN PHOSPHORIC ACID SOLUTIONS¹

ALFRED J. STAMM AND WILBY E. COHEN²

*Forest Products Laboratory,³ Forest Service, U. S. Department of Agriculture,
Madison, Wisconsin*

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INTRODUCTION

Perhaps the best physical means of characterizing cellulose for industrial use is the determination of the viscosity of its solutions. Unfortunately, there are no true physical solvents for cellulose itself, although there are such solvents for cellulose derivatives. Cuprammonium solution perhaps comes the closest to being a true physical solvent, and it is for this reason that it is almost exclusively used in viscosity studies. Cuprammonium solution, however, is subject to several variations which may affect its solvent power and the nature of the cellulose dispersion: (1) the total copper ammonia complex concentration, (2) the relative proportions of copper and ammonia, (3) the portion of the copper (10) which exists as colloidal copper hydroxide, (4) the amount of sugar added to the solvent to stabilize the system, (5) the extent to which the ammonia is oxidized to nitrites in making the solvent, and (6) the extent to which the solvent is exposed to air in the preparation and study of the cellulose solutions. Because of these possible variations, it is not surprising that considerable difference of opinion has been expressed at recent chemical meetings as to the nature of the dispersion of cellulose in cuprammonium solvent. Farr (5) contends that the cellulose is not molecularly dispersed as many believe, but is broken down into elliptical particles similar to those which she obtained by treating cellulose with various acids (6, 7). In this case the particles, which do not deviate appreciably from spherical, would have but a slight effect upon the viscosity, as she contends. Farr believes that it is the solution of the pectic film of the cotton, rather than the cellulose itself, which is largely responsible for the viscosity (5).

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² Commonwealth Fellow, 1935-37, Division of Forest Products, Council for Scientific and Industrial Research, Melbourne, Australia.

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Staudinger (12, 14), on the other hand, believes that cellulose in cuprammonium solvent is dispersed in the form of long macromolecular chains similar to many other polymeric materials, including cellulose derivatives in organic solvents. Staudinger's views are supported by a number of different investigators (8). It seemed highly probable to the authors that both Farr and Staudinger might be right, the difference resting on differences in the cuprammonium solvent used by each of the investigators. It thus seemed desirable to try to find a solvent for cellulose that was not subject to the foregoing variations. A preliminary survey indicated that concentrated phosphoric acid was the most promising solvent. It is true that this is a hydrolytic solvent, but hydrolysis takes place slowly enough to make possible viscosity measurements on the solutions after the cellulose has been in solution for different intervals of time. Extrapolation of the resulting relationship between viscosity and time to zero time gives the viscosity of the undegraded cellulose.

PREPARATION OF SOLUTIONS

A simple means of preparing cellulose solutions of known concentration in phosphoric acid was first sought. It was soon learned that undegraded cellulose cannot be completely dispersed in concentrated phosphoric acid without the use of some water. Apparently the cellulose must be swollen in water and the concentration of the acid built up gradually to get complete solution. This is in agreement with the findings of Ekenstam (3), who has recently claimed that cellulose forms an oxonium compound $(C_6H_{10}O_5 \cdot 2H_2O \cdot H_3PO_4)_n$, with two molecules of water and one of acid per glucose anhydride group, which is soluble in concentrated phosphoric acid.

The procedure finally adopted for preparing the solutions of known concentration was as follows: Accurately weigh 10 to 30 mg. of air-dry cellulose of known moisture content into a small agate mortar. Add 1 cc. of water and gently macerate with an agate pestle. Add phosphoric acid (85 to 100 per cent) drop by drop, working with the pestle between additions. When the swollen cellulose is almost completely dissolved, the acid may be added more rapidly. Wash the cellulose solution into a weighed beaker with concentrated phosphoric acid. Add phosphoric acid until the desired concentration of cellulose is obtained and weigh. Filter the solution through a No. 3 Jena fritted glass filter to remove any trace of foreign matter that might clog the viscometer. Remove air from the solution with a vacuum pump at room temperature. The preparation of the solution from the time the cellulose begins to dissolve to the time of complete removal of air generally takes from 20 to 30 min.

Solutions prepared in this way, even when the filtering step was omitted, were found to be practically void of microscopically visible particles, in-

dicating that the cellulose is not dispersed as Farr elliptical particles (5, 6, 7).

VISCOSITY MEASUREMENTS

The viscosity measurements were made in a Bingham viscometer with a capillary bore of 0.0337 cm., a capillary length of 10.1 cm., and a bulb capacity between reading marks of 3.995 cc. The viscometer was securely clamped in place in a thermostatically controlled water bath held at $25^{\circ}\text{C.} \pm 0.002^{\circ}$. The applied air pressure was controlled with a reducing valve followed by one to four air-escape bubblers containing sulfuric acid, which were connected in series with each other and in parallel with the line to the viscometer. The air-pressure valve was set so that a constant but not too rapid rate of bubbling occurred through the bubblers. In this way the air pressure was controlled during a single measurement to 0.01 cm. of mercury, as was indicated by a mercury manometer that was read with a cathetometer. The readings could be reproduced in subsequent measurements to 0.03 cm. of mercury.

It would be practically impossible to prepare a phosphoric acid solution of exactly the same concentration as that serving as solvent for the cellulose. Fortunately, the viscosity of the solvent, which is required to calculate the specific viscosity of the cellulose, can be obtained by a simpler means (2). After completing the viscosity measurement on the solution, the solution can be heated in the viscometer to complete the hydrolysis of the cellulose to glucose and other final hydrolysis products. This avoids an extra cleaning and filling of the viscometer. Concentrations of hydrolysis products of 0.1 per cent and less will affect the viscosity of the phosphoric acid less than 0.25 per cent. If more accurate results are desired, the viscosity can be corrected for the presence of the hydrolysis products with an error of less than 10 per cent, using the Einstein viscosity equation (2).

Preliminary tests indicated that when the solutions of cellulose in phosphoric acid were heated in boiling water for half an hour or more to complete the hydrolysis, the solution developed a slight straw color and the viscosity of the solution after cooling to 25°C. increased for several days. Tests were made on solutions of 1 per cent glucose in phosphoric acid prepared in the same way as the cellulose solutions. The viscosity increased as much as 5 per cent in two days after heating to 100°C. for an hour. The change that occurs is so slow that the first viscosity value obtainable after cooling is but very slightly greater than the original viscosity before heating. Apparently the heating causes a caramelization which consists of a slow polymerization to chain molecules. This polymerization requires heat to initiate the reaction but is capable of continuing after cooling. When the solutions of glucose in phosphoric acid were not heated

above 60°C. no discoloration resulted, nor was an increase in viscosity obtained. The solutions of cellulose in phosphoric acid were thus heated to 50° to 60°C. for several hours to insure complete hydrolysis and yet to avoid subsequent polymerization. Figure 1 shows the viscosity in terms of the applied pressure multiplied by the efflux time for phosphoric acid of different concentrations and hydrolyzed solutions of cellulose in phosphoric acid plotted against the acid concentration for two different applied pressures on the viscometer. The curves indicate that within experimental error the hydrolyzed solutions have the same viscosity as the solvent.

The measurements were made on a cotton linters alpha cellulose (99.6 per cent alpha) and a normal spruce sulfite pulp and the same after beating

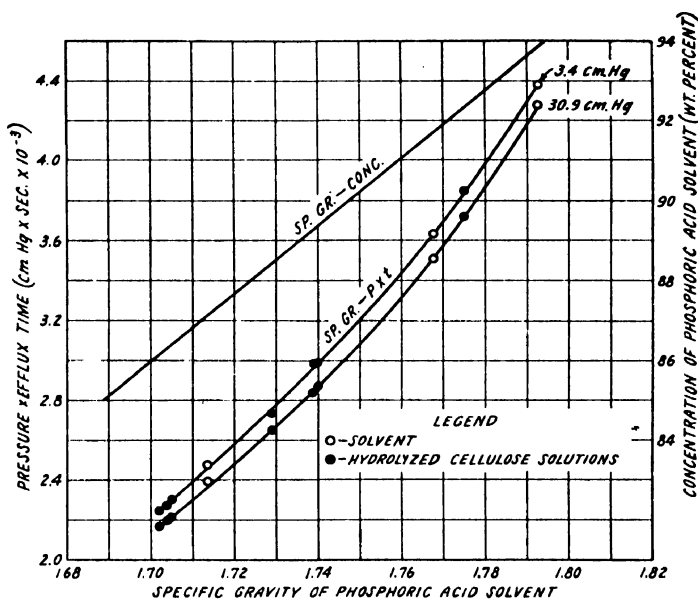


FIG. 1. Product of pressure and efflux time for phosphoric acid solutions of different specific gravity and concentration and the same containing hydrolyzed cellulose for two different applied pressures on the viscometer.

for 20 hr. in a rod mill. The concentrations used ranged from 0.000077 to 0.00099 g. per cubic centimeter (0.00048 to 0.0061 units of glucose anhydride per liter). The viscosity measurements were made at 30.9, 20.5, 10.3, and 3.4 cm. of mercury pressure on each of the solutions in the order given, a measurement from left to right and from right to left being made at each pressure. The average of these two times of efflux was used in the viscosity calculations. The mean time between starting the first measurement and ending the second was taken for calculating the time that the cellulose had been in solution. The agreement between the readings taken in the two directions was quite good when an interval of 2 min. was allowed between measurements for drainage of the viscous phosphoric acid,

except for the initial readings where the viscosity was changing very rapidly with time. Although this short pause between measurements eliminates any difference in drainage between back and forth measurements at a single pressure, there is an unavoidable drainage difference between measurements made under different pressures.

Figure 2 gives the relationship between the product of the applied pressure and efflux time under different applied pressures plotted against the logarithm of the efflux time in seconds for completely hydrolyzed cellulose in 86.15 and 86.40 per cent phosphoric acid. When the efflux time is doubled the pressure-efflux time product is increased about 1.2 per cent.

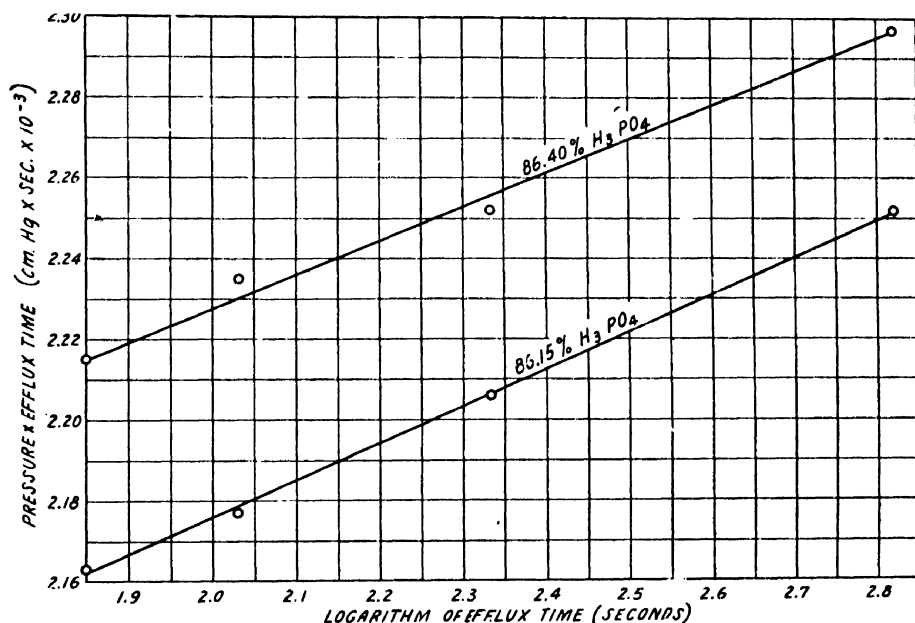


FIG. 2. Product of pressure and efflux time versus the logarithm of the efflux time for hydrolyzed cellulose solutions in two different concentrations of phosphoric acid.

The maximum time of efflux variation between the first measurement and the final hydrolyzed value for the most concentrated solution of cellulose used was 75 per cent. This would result in a viscosity error of 0.9 per cent, due to the drainage factor. In the case of solutions containing less than 0.0003 g. of cellulose per gram of acid, the error was less than 0.25 per cent. As the viscosity values of chief interest are those for the more dilute cellulose solutions, no attempt was made to make a drainage correction.

The specific viscosity η_{sp} (the increase in relative viscosity caused by the solute) per unit concentration in grams per cubic centimeter is plotted against the time the cellulose has been in solution in figures 3 and 4 for

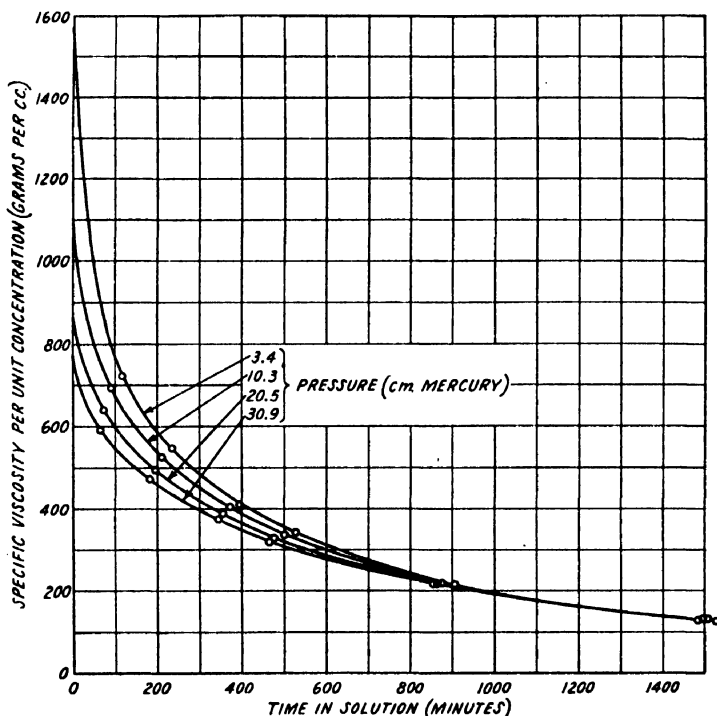


FIG. 3. Specific viscosity per unit concentration for a 0.000557 g. per cubic centimeter solution of unbeaten pulp in an 88.4 per cent phosphoric acid solution versus time in solution for different applied pressures on the viscometer.

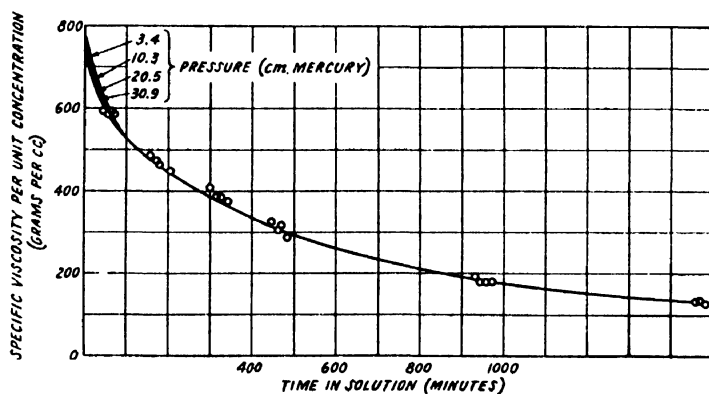


FIG. 4. Specific viscosity per unit concentration for a 0.000979 g. per cubic centimeter solution of unbeaten pulp in an 89.4 per cent solution of phosphoric acid versus time in solution for different applied pressures on the viscometer.

unbeaten pulp solutions containing 0.000557 and 0.000979 g. of pulp per cubic centimeter, respectively. The specific viscosity per unit concentration, η_{sp}/c , increases with a decrease in the applied pressure used in making

the viscosity measurements for the higher η_{sp}/c values. The divergence of the η_{sp}/c values obtained at different applied pressures increases with an increase in the concentration of cellulose in solution. The apparent reason for this is that in concentrations sufficiently great for interference between the elongated cellulose molecules the interference is decreased with increasing velocity of shear, owing to the increased orientation of the molecular chains. This will be considered further in the next section.

MOLECULAR WEIGHT AND LIMITING CONCENTRATION OF CELLULOSE

The apparent molecular weights of the pulp in different concentrations, determined under different applied pressures and for different lengths of time that the cellulose has been in solution, were calculated from the data of figures 3 and 4 and the corresponding data for other concentrations of the unbeaten pulp, the beaten pulp, and the cotton linters alpha cellulose, using the relationship of Staudinger (12):

$$M = \frac{\eta_{sp}}{c} \frac{0.162}{K_m} \quad (1)$$

in which M is the molecular weight of the cellulose, η_{sp} is its specific viscosity, 0.162 is a factor to transpose the concentration c in grams per cubic centimeter to glucose anhydride units per liter, and K_m is the Staudinger proportionality constant. The constant K_m used in the following calculations is 11.8×10^{-4} at 25°C. This was obtained by a linear extrapolation of Ekenstam's (3) values, $K_m = 12.4 \times 10^{-4}$ at 20°C. and $K_m = 14.7 \times 10^{-4}$ at 0°C. Staudinger (13) gives a value for K_m of 18.0×10^{-4} at 20°C., which is larger. Further work on the molecular weight of cellulose in phosphoric acid solutions by other methods will have to be done before a more exact value for K_m can be obtained. Until then the actual molecular weight values can be considered only as approximate. The relative molecular weight values should be considerably more accurate, however, over the molecular weight range considered.

The apparent molecular weights of the undegraded celluloses (zero time in solution) for the different concentrations and different applied pressures are shown in figure 5 for the pulp and in figure 6 for the alpha cellulose. The apparent molecular weight varies but slightly with concentration over the range studied for the higher applied pressures on the viscometer, but increases appreciably with concentration for the lower pressures. The molecular weights of the beaten and the unbeaten pulp are identical within experimental error. Over the range studied (86 to 92 per cent) the concentration of phosphoric acid has no effect. The practical limiting concentration above which molecular interference appreciably affects the viscosity and the calculated molecular weight is thus dependent not only upon the molecular weight and the concentration of the cellulose solution,

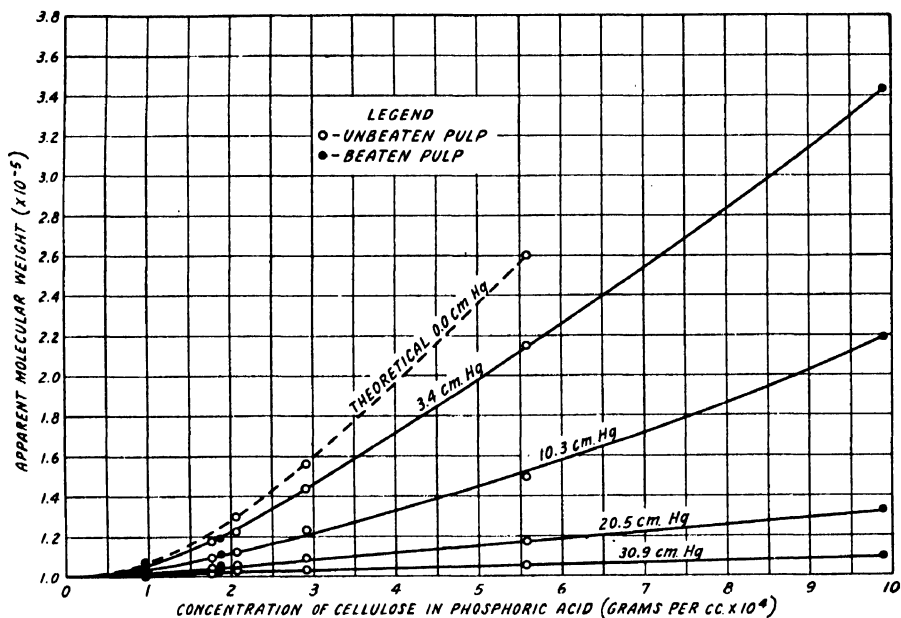


FIG. 5. Apparent molecular weight of beaten and unbeaten pulp versus the concentration of the pulp in phosphoric acid solution for different applied pressures on the viscometer.

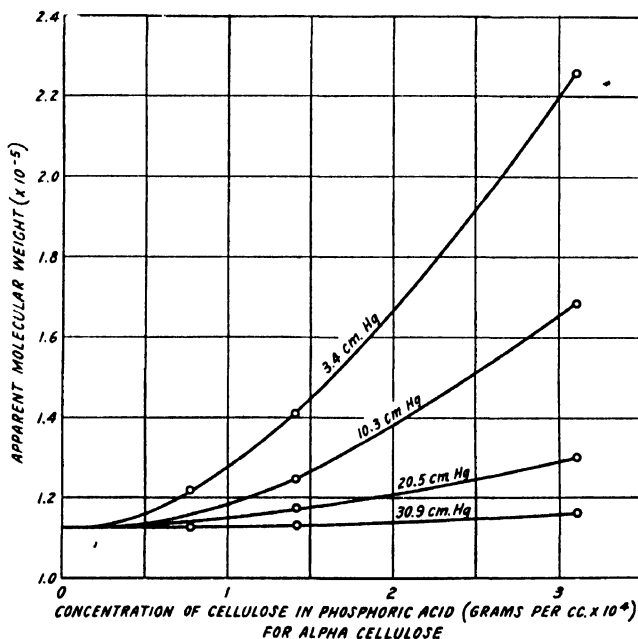


FIG. 6. Apparent molecular weight of cotton linters alpha cellulose versus the concentration of the cellulose in phosphoric acid solution for different applied pressures on the viscometer.

but also on the velocity of shear under which the measurements are made. The theoretical curve in figure 5 for the apparent molecular weights at the limiting value of zero applied pressure was obtained by plotting the apparent molecular weight against the applied pressure on the viscometer for different concentrations and extrapolating to zero pressure. The curves for the different applied pressures in figures 5 and 6 converge at a moisture content below 3×10^{-5} g. of cellulose per cubic centimeter. This limiting concentration can be more accurately estimated from figure 7, in which the limiting molecular weight values for the partially hydrolyzed pulps (corresponding to the points on curves of the type of figures 3 and 4 above which

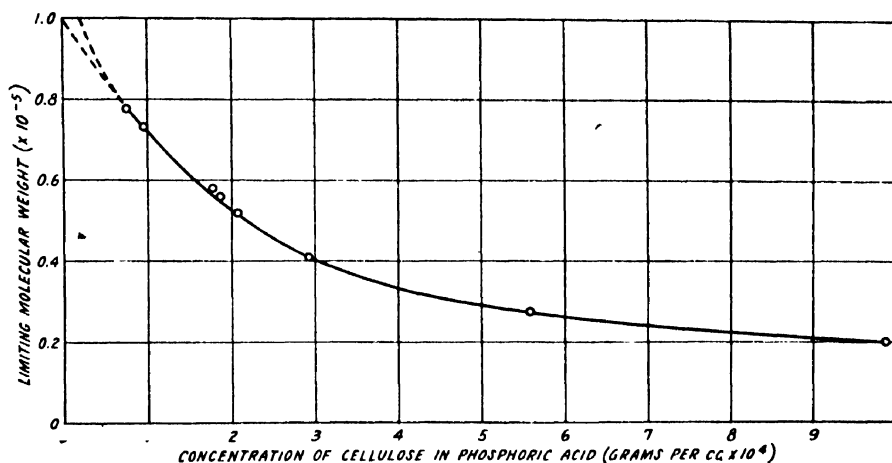


FIG. 7. Limiting molecular weights of partly hydrolyzed pulp above which the values are affected by the applied pressure on the viscometer versus the concentration of the pulp in phosphoric acid solution.

the η_{sp}/c values for different applied pressures diverge) are plotted against the pulp concentration. From this figure the limiting concentration appears to be less than 2×10^{-5} g. of cellulose per cubic centimeter for a molecular weight of 100,000.

This limiting concentration is practically equal to the theoretical value for packed spheres, calculated upon the assumption that the limiting volume of uninterfered motion of the elongated molecules is a sphere with the long axis of the molecule equal to the diameter. The pulp with a molecular weight $M = 100,000$ on a phosphoric acid-free and water-free basis, and $M_1 = 183,000$ on a hydrated and phosphated basis (4), has a degree of polymerization of 618, and a length, l , of 3180 Å. (5.15 Å. per glucose anhydride unit). The limiting concentration C on this basis is given by the equation

$$C = \frac{6\dot{M}_1}{\pi l^3 A} \quad (2)$$

in which A is the number of molecules in a gram molecule. This gives a value of 1.8×10^{-5} g. per cubic centimeter for the limiting concentration. A limiting concentration of the same order of magnitude is obtained on the basis of the limiting volume of uninterfered motion of elliptical molecules increasing, according to Onsager (9), as the square of the ratio of the major to the minor axis. This gives a limiting volume 1.5 times that obtained on the limiting sphere of action basis (11) and a limiting concentration 33 per cent less or 1.2×10^{-5} g. per cubic centimeter. Both of these values are within the range of accuracy of the experimental value.

The velocity of efflux under the different applied pressures was calculated from the viscometer dimensions and the theoretical time of efflux for the cellulose in solution for an infinitesimal length of time. These data indicate that over the concentration and applied pressure range used molecular weight values can be calculated with an accuracy of 5 to 10 per cent whenever the efflux velocity exceeds 10 to 12 cm. per second. Molecular weight values can thus be determined with a fair degree of accuracy at concentrations appreciably greater than the limiting concentration for velocities of shear approaching zero by increasing the velocity of shear sufficiently to reduce molecular interference as a result of molecular orientation. Because of this Staudinger (12) has been able to determine molecular weights of cellulose in concentrations of several tenths of a per cent.

HYDROLYSIS CONSTANT OF CELLULOSE

The viscosity measurements of cellulose dissolved in phosphoric acid furnish the data for calculating not only the molecular weight of cellulose but also the hydrolysis constant of cellulose. Ekenstam (4) has derived the following equation for calculating the hydrolysis constant:

$$K = \frac{1}{t} \ln \frac{1 - \frac{m}{M}}{1 - \frac{m}{M_t}} \quad (3)$$

where t is the time, M the initial molecular weight, M_t the average molecular weight after time t , and m is the final molecular weight. When M and M_t are large compared to m this equation can be simplified to

$$K = \frac{m}{t} \left(\frac{M - M_t}{MM_t} \right) \quad (4)$$

The molecular weight of the final hydrolysis product m dissolved in phosphoric acid is 240, according to Ekenstam (4). Table 1 gives the hydrolysis constant when t is expressed in minutes for the unbeaten pulp, beaten pulp, and cotton linters alpha cellulose calculated from equation 4, using

TABLE 1
Hydrolysis constants of cellulose dissolved in concentrated phosphoric acid at 25°C.

MATERIAL	CONCENTRATION		TIME IN SOLUTION	MOLECULAR WEIGHT	HYDROLYSIS CONSTANTS	
	Cellulose	H ₂ PO ₄			Individual values × 10 ⁶	Average values 4 to 24 hr. × 10 ⁶
	<i>grams per cc.</i>	<i>per cent</i>	<i>hours</i>			
Unbeaten pulp.....	0.000557	89.3	0	105,500		
			2	72,000	8.83	
			3	65,100	7.84	
			4	59,600	7.30	
			6	50,600	6.85	
			8	43,200	6.83	
			10	37,400	6.90	
			12	33,200	6.89	
			16	26,900	6.93	
			20	22,600	6.96	
			24	19,200	7.10	6.97
	0.0000979	89.4	0	100,000		
			2	70,000	8.58	
			3	63,000	7.83	
			4	57,600	7.36	
			6	48,700	7.03	
			8	41,150	7.15	
			10	35,650	7.22	
			12	31,550	7.23	
			16	25,100	7.46	
			20	21,400	7.35	
			24	18,500	7.35	7.27
	0.000293	88.4	0	102,700		
			24	19,200		6.89
	0.000206	86.1	0	102,700		
			24	18,800		7.23
	0.000178	92.3	0	101,300		
			24	17,400		7.18
Beaten pulp.....	0.000989	86.4	0	109,600		
			24	21,550		6.77
	0.000188	86.1	0	102,700		
			24	18,900		7.07
Cotton linters alpha cellulose.....	0.000311	86.3	0	116,500		
			24	23,850		5.67
	0.000142	86.4	0	113,700		
			24	23,850		5.79
	0.0000766	86.3	0	113,000		
			24	23,300		5.58

Ekenstam's value for m . The individual hydrolysis constant values calculated for various intervals of time, from 0 to 24 hr., that the cellulose is in solution, are given for the two concentrations of unbeaten pulp shown in figures 3 and 4, together with the average value for 4 hr. through 24 hr. In the case of the other concentrations of unbeaten pulp, beaten pulp, and cotton linters alpha cellulose only the average values are given. The individual values for these solutions are similar to the individual values given in that they are constant within experimental error after the first 4 to 6 hr. Ekenstam (2, 4) obtained similar high initial values for some of his cellulose samples. The beaten and unbeaten pulps have the same hydrolysis constant within experimental error. The hydrolysis constants of the pulps are larger than for the cotton linters alpha cellulose, as would be expected, because they undoubtedly contain more readily hydrolyzable carbohydrates.

SUMMARY

Cellulose can be completely dissolved in concentrated phosphoric acid to form dilute solutions void of microscopically visible particles when the cellulose is first swollen in water and the acid concentration built up gradually. Viscosity measurements on these solutions after different times in solution and under different applied pressures were made. The viscosity of the solvent was shown to be equal to the viscosity of the dilute cellulose solutions after completely hydrolyzing for 1 hr. at 50° to 60°C. Hydrolysis at 100°C. initiates a slow polymerization of glucose dissolved in phosphoric acid which continues for days. The limiting concentration of cellulose above which molecular interference occurs when the viscosity measurements are made under a low rate of shear is about 2×10^{-6} g. per cubic centimeter. This is practically equal to the concentration in which spheres described about the long axis of the molecules are packed. When the viscosity is determined under higher rates of shear, higher concentrations can be used in molecular weight determinations because of the molecular orientation. The molecular weights of a highly beaten pulp and of the unbeaten pulp calculated from these data are both 100,000 on a water- and acid-free basis. The corresponding value for a cotton linters alpha cellulose is 113,000. Hydrolysis constants for cellulose in phosphoric acid calculated from these data are quite constant after the first 4 hr. in solution. The average hydrolysis constants for the pulp and for the cotton linters alpha cellulose are 7.05×10^{-6} and 5.68×10^{-6} , respectively, after the first 4 hr.

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OPTICAL PROPERTIES OF SOLUTIONS OF TOBACCO MOSAIC VIRUS PROTEIN¹

MAX A. LAUFFER

The Rockefeller Institute for Medical Research, Princeton, New Jersey

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INTRODUCTION

Tobacco mosaic virus nucleoprotein was first obtained in crystalline form by chemical means by Stanley in 1935 (13), from the juice of Turkish tobacco plants infected with tobacco mosaic virus. All of the evidence available at present indicates that the active disease-causing agent is this nucleoprotein (14). The results of recent studies indicate that the virus nucleic acid closely resembles yeast nucleic acid, that it is in combination with protein, and that it is necessary for virus activity (1, 9). Because the virus protein has an extremely high molecular weight, a value in the millions (3, 7, 20), it is possible to obtain very superior preparations by differential centrifugation (20). The protein is insoluble at its isoelectric point and in 20 per cent ammonium sulfate solution. It crystallizes in small needle-shaped crystals, visible only with the microscope. Bernal and Fankuchen have studied the x-ray diffraction patterns of the virus protein in many states, and they concluded from their findings that these crystals are in the mesomorphic or paracrystalline state, rather than in the true crystalline state (2). These crystals are, nevertheless, definite solid objects, visible with the microscope, and, inasmuch as crystallinity of any kind is not an infallible criterion of protein purity, the crystallinity of the tobacco mosaic virus protein is probably not much less significant as a criterion of purity than that of other proteins.

DOUBLE REFRACTION OF FLOW

Takahashi and Rawlins (16) first showed that the juice from tobacco plants diseased with tobacco mosaic exhibited stream double refraction, and it has since been demonstrated that the solutions of the purified tobacco mosaic virus protein show the phenomenon to a marked degree (1, 8, 17). The question of the interpretation of this double refraction was recently considered in some detail, and it was concluded that the

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phenomenon was due in this case to the orientation of rod-like protein particles in the flowing stream (8). These rod-shaped particles may themselves be either optically isotropic or anisotropic. Wiener (19) has shown from theoretical considerations that a system composed of very small isotropic rods arranged parallel to each other in an isotropic medium of different refractive index is optically anisotropic. It behaves like a uniaxial crystal with the optic axis in the direction of orientation. The following equation, which represents the double refraction of such a system, may be derived from Wiener's considerations (8):

$$N_e^2 - N_o^2 = \frac{V_1 V_2 (N_1^2 - N_2^2)^2}{(V_1 + 1)N_2^2 + V_2 N_1^2} \quad (1)$$

N_e and N_o are the indices of refraction of extraordinary and ordinary rays, respectively, N_1 and N_2 the refractive indices of rods and medium

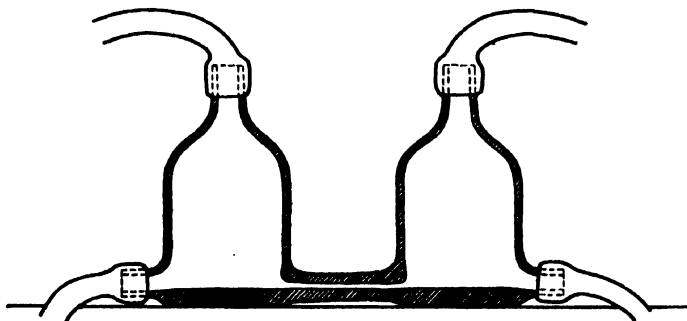


FIG. 1. Picture diagram of streaming cell

respectively, and V_1 and V_2 their respective relative volumes. It is readily apparent from this equation that, if $N_1 = N_2$, one obtains no double refraction. If $(N_e - N_o)$ is plotted against N_2 , a parabola is obtained with a minimum at the point $N_2 = N_1$. If rod-shaped particles are oriented in a medium with a refractive index equal to their own, the system should show no double refraction of this sort,—i.e., no morphic double refraction. Any double refraction shown by the system under such conditions must be the intrinsic double refraction of the particles themselves. This point was considered by Freundlich (4). Steubel (15) evaluated the intrinsic and morphic double refraction shown by cross-striated muscle by measuring the double refraction of the muscles immersed in various solvents of different refractive index. This method has been applied to stream double refraction by Signer (12) in his studies on polystyrene solutions.

By measuring stream double refraction of tobacco mosaic virus protein in solvents of different refractive indices, such as various glycerol-water mixtures and aniline-glycerol-water mixtures, the effect of the refractive

index of the medium on the double refraction of flow was determined. The apparatus used for this measurement consisted of a streaming cell and a polarizing microscope fitted with a photoelectric tube and a vacuum tube amplifying system, as described previously (8). The change in plate current caused by the flow of the liquid, as measured by galvanometer displacements in millimeters, was taken as a measure of stream double refraction. The streaming cell used in this case differed from that described in the original study. As may be seen in figure 1, it consisted of a glass capillary fused to two reservoirs, so arranged that all of the liquids studied could be made to flow at the same constant pressure. By this means the reduced rate of flow compensates for the increased viscosity of the less fluid solvents, and the mechanical force exerted on the suspended

TABLE 1

Double refraction of flow of tobacco mosaic virus protein (1.08 mg. per cubic centimeter) in solvents of different compositions

	COMPOSITION OF SOLVENT IN VOLUME PER CENT			REFRACTIVE INDEX	STREAM DOUBLE REFRACTION EXPRESSED AS MILLIMETERS OF GALVANOMETER DEFLECTION
	Water	Glycerol	Aniline		
1	100	0	0	1.334	54
2	80	20	0	1.362	42
3	60	40	0	1.389	33
4	50	50	0	1.402	27
5	30	70	0	1.430	23
6	20	80	0	1.442	19
7	10	90	0	1.454	14
8	2	88	10	1.477	6.0
9	2	68	30	1.503	4.5
10	2	48	50	1.526	2.4
11	2	28	70	1.55	0

rods remains constant. It may be seen from table 1 and figure 2 that the double refraction of flow decreases greatly as the refractive index of the medium approaches 1.6, the approximate value of the refractive index of the tobacco mosaic virus protein. This value was calculated from the refractive index of a 1.78 per cent solution of the protein, $N_D^{25^\circ} = 1.33715$, and that of the solvent, $N_D^{25^\circ} = 1.33405$, using the equation presented by Wiener (19),

$$N_m^2 = \frac{(1 + V_1)N_1^2 + (1 - V_1)N_2^2}{(1 - V_1)N_1^2 + (1 + V_1)N_2^2} \times N_1^2 \quad (2)$$

where N_m is the refractive index of the solution and the other symbols have the same meaning as in equation 1.

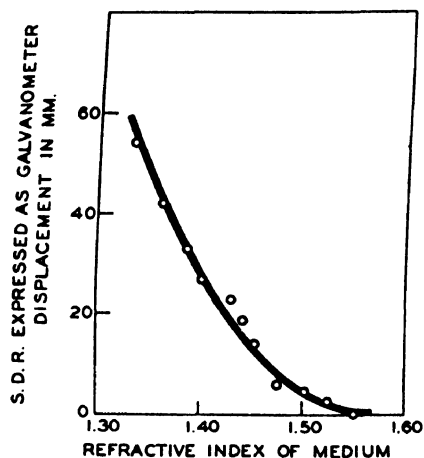


FIG. 2. The dependence of the stream double refraction of tobacco mosaic virus protein upon the refractive index of the solvent.

TABLE 2

The effect of various solvents on the activity of tobacco mosaic virus protein as measured by the half-leaf method on Phaseolus vulgaris

	1	2	3
Composition of solvent in volume per cent:			
Water.....	10	2	2
Glycerol.....	90	88	48
Aniline.....	0	10	50
Concentration of virus in contact with solvent.....	10 mg. per cc.	10 mg. per cc.	10 mg. per cc.
Time of contact with solvent...	7 days	10 min.	10 min.
Concentration of virus in M/10 phosphate at time of inoculating.....	10^{-6} g. per cc.	10^{-7} g. per cc.	10^{-7} g. per cc.
Number of half-leaves inoculated.....	38	26	26
Average number of lesions per half-leaf (\bar{X}).....	111.5	8.1	5.6
Average number of lesions per half-leaf for control at same concentration (\bar{Y}).....	131.8	6.8	6.5
Standard error of $\bar{X} - \bar{Y}$ ($SE_{\bar{X} - \bar{Y}}$).....	9.52	0.89	0.90
$(\bar{X} - \bar{Y})/SE_{\bar{X} - \bar{Y}}$	2.13	1.5	1.0

The control in each case was a sample of virus protein in water from the same batch as that exposed to the solvent under consideration. It was diluted directly from water solution. $(\bar{X} - \bar{Y})/SE_{\bar{X} - \bar{Y}}$ is a test for the significance of the difference of the number of lesions per half-leaf shown by sample and corresponding blank. By convention, if this quantity exceeds 2.1, the difference is regarded as being due to factors other than experimental error. These results indicate that 1 week's contact with glycerol causes a slight decrease in virus activity, whereas 10 minutes' contact with the other solvents causes no significant change in virus activity.

In table 2 are presented the results of activity measurements made on virus protein samples which had been dissolved in the solvents employed in the present study for periods of time great enough to allow double refraction measurements to be made. It is seen that no appreciable loss in activity results from this treatment. Since activity in the biological sense is a very sensitive measure of change in the protein molecule, it must be concluded that the reduction in double refraction of flow can not be attributed to denaturation or destruction of the protein by the solvents. This conclusion may be checked more directly for the case of the protein dissolved in glycerol-water solvents. It was found that, when solutions of the virus protein in 90 per cent glycerol were diluted with water, the double refraction per unit concentration of protein increased to the value obtained originally for a solvent of the same composition as that obtained upon dilution. This shows that the effect of the solvent is a reversible one, a necessary condition for an effect due to nothing but the refractive index of the solvent. In view of the facts that the property of stream double refraction shown by the virus protein is lost when the protein is dissolved in a medium whose refractive index is the same as that of the protein and that this effect seems not to be due to any change in the protein, it is evident that the double refraction of flow of the tobacco mosaic virus protein solutions is due largely, if not entirely, to the effect of the shape of the particles and scarcely, if at all, to the intrinsic double refraction of the particles themselves. This fact, as will be seen presently, is of great importance to those who are interested in the nature of plant viruses.

THE LIQUID CRYSTALLINE STATE

The liquid crystalline or paracrystalline state is encountered in many biological systems (5). As will be seen presently, relatively concentrated solutions of the tobacco mosaic virus protein afford an example of such systems, for they may exist in a state which can be described as two-component liquid crystalline. The jelly-like pellets obtained by ultracentrifuging solutions of the virus protein may be regarded as being very concentrated colloidal solutions. Figure 3 is a photomicrograph of a flattened section of the jelly-like material constituting a pellet of the ultracentrifuged tobacco mosaic virus protein, taken with a polarizing microscope. This picture resembles those obtained in a similar manner with substances known to be liquid crystalline or paracrystalline, for example, wetted bromophenanthrenesulfonic acid (11). Furthermore, the x-ray diffraction pattern shown by these pellets may be interpreted as being that of a paracrystalline material (2, 21). It would seem, then, that these jelly-like pellets are true examples of the paracrystalline state. As a result of his studies with a great number of organic compounds, Vorlander (18) has come to regard the ability to exist in the liquid crystalline

state as being associated with materials having rod-shaped molecules. This generalization may be carried over from systems of one component to systems of two components, such as tobacco mosaic virus protein in water or bromophenathrenesulfonic acid in water. This paracrystallinity of the tobacco mosaic virus protein pellet, then, must be regarded as constituting additional evidence of the rod-like character of the tobacco mosaic virus protein.

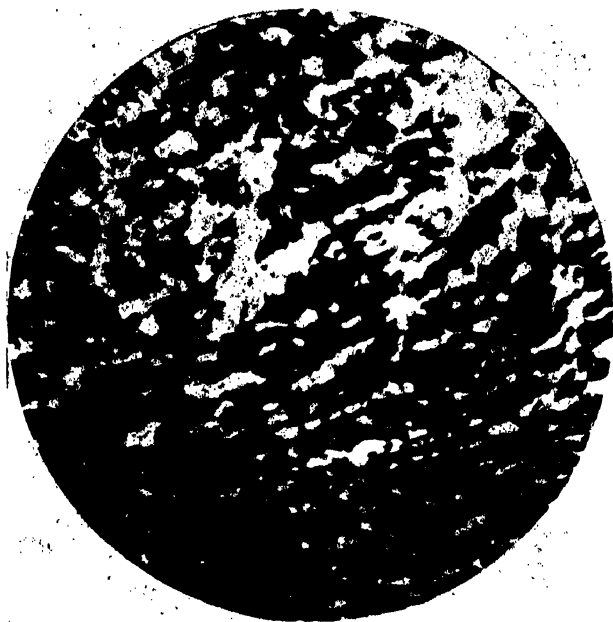


FIG. 3

FIG. 3. Photomicrograph of a flattened section of a tobacco mosaic virus protein pellet obtained by ultracentrifugation, taken with the aid of a polarizing microscope. $\times 135$. (Photograph by J. A. Carlile.)

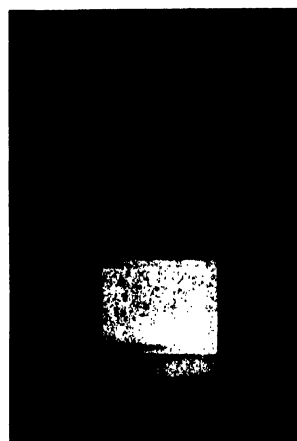


FIG. 4

FIG. 4. A solution of tobacco mosaic virus protein following separation into two layers. Photographed between crossed Polaroid plates. (Photograph by J. A. Carlile.)

THE LAYERING PHENOMENON AND DEPOLARIZATION OF SCATTERED LIGHT

When relatively concentrated solutions of tobacco mosaic virus protein are allowed to stand, they separate into two layers, the bottom one of which is spontaneously birefringent or liquid crystalline (1, 8). Figure 4 is a picture of such a system, photographed between crossed Polaroid plates. Insofar as it is known, these two layers differ chemically only in that the concentration of protein is greater in the bottom layer (1). The light-scattering properties of these two layers differ considerably. The light scattered perpendicularly by a colloidal solution with a disperse

phase consisting of very small isotropic spheres is completely polarized, with the electrical vector in the plane perpendicular to that defined by the incident beam and the direction of observations. However, if the disperse phase consists of very small anisotropic or asymmetrical particles, even though the incident light is polarized, the scattered light will be depolarized;

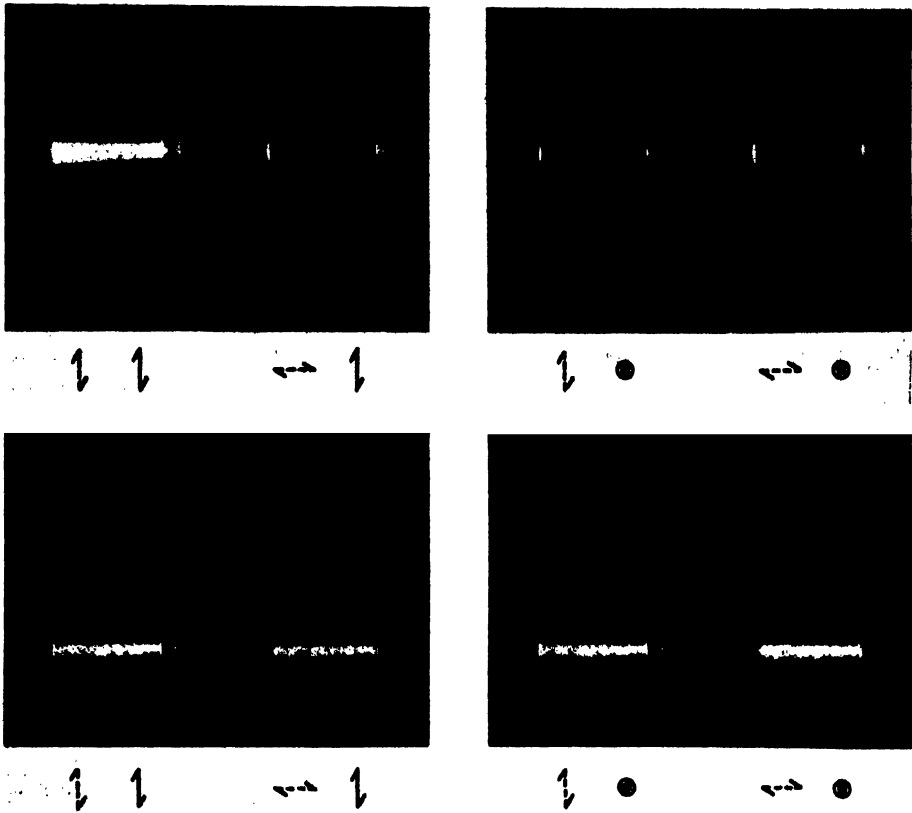


FIG. 5. The depolarization of the light scattered by the top and bottom layers (figure 4). The incident beam enters the cell at the right and leaves on the left. The solid symbols indicate the plane in which the electrical vector of the incident light is vibrating and the broken symbols represent the plane of vibration of the observed scattered light. The point enclosed by the circle is a symbol indicating that the vibrations are in a plane perpendicular to that of the paper. (Photographs by J. A. Carlile.)

that is, it will have electrical components in both the plane of incidence and that perpendicular to it. If the particles of the disperse phase are large and the incident light is unpolarized, there will be an apparent depolarization of the scattered light, even though the particles are spherical and isotropic (6). Figure 5 shows the horizontal and vertical components of the scattered light for both layers for incident beams vibrating hori-

zontally and for those vibrating vertically. The results for the top layer may be analyzed roughly by the method of Krishnan (6). The intensity of the scattered light is the sum of several terms: (A) a vertical component due to the size of the particles, (B) a horizontal component due to size, (C) a vertical component due to shape or anisotropy, and (D) a horizontal component due to shape or anisotropy.

In the case under consideration, when the incident light vibrates in the vertical plane, the vertical component of the scattered light is much greater than the horizontal component (figure 5, upper left). This light can be pictured as consisting of a relatively intense effect due to (A) as described above, no effect due to (B), a small horizontal component due to (D), and another small vertical component due to (C), which, on theoretical grounds, should be four-thirds as intense as the component due to (D). When the incident light vibrates in the horizontal plane, the scattered light consists of a relatively weak horizontal component and an essentially equal vertical component (figure 5, upper right). (A) and (B) may be thought to contribute little to the light scattering in this case, the vertical component being due largely to (C) and the horizontal component due largely to (D). In this case, on theoretical grounds, (C) should equal (D). These results show that the depolarization exhibited by the upper layer is due to anisotropy or asymmetry of the dispersed particles, rather than to size beyond the critical range. This conclusion is entirely in harmony with that drawn from the other observations discussed. In the bottom layer, on the other hand, scattered light is seen to be largely depolarized regardless of the condition of polarization of the incident light (figure 5, bottom). This is to be expected, because the bottom layer as a whole exhibits birefringence without extinction directions (8), and, therefore, the scattered light regardless of its state of polarization immediately after being scattered is largely depolarized while passing out through the solution.

An examination of figure 6, which is a photomicrograph of a droplet of the bottom layer material, taken with the aid of a polarizing microscope, reveals directly that this bottom layer is in the liquid crystalline or paracrystalline state. It has been visualized as consisting of "a three-dimensional mosaic of regions arranged at random to each other, but in each of which all the rod-shaped particles will lie approximately parallel" (1). We now know that these rod-shaped virus molecules or particles have very little or no intrinsic double refraction. The double refraction of the anisotropic region is, then, of the type discussed by Wiener,—a system consisting of small isotropic rods arranged parallel in an isotropic medium of different refractive index. These small doubly refracting volumes resemble to a considerable extent certain living cells known to exhibit double refraction, for example, the head of the sperm of the cuttlefish. This living cell

probably contains nucleoprotein in the paracrystalline state (11). The question of whether plant virus protein particles should be regarded as being essentially living organisms or essentially unusual chemical individuals is not yet considered closed. It has been suggested by Rawlins and Takahashi (10) that the property of double refraction of flow and the related phenomenon of liquid crystallinity shown by plant virus nucleoproteins may indicate that these viruses are small living organisms composed of nucleoproteins in the paracrystalline state, analogous to the sperm heads just mentioned. The present finding, that these rod-shaped virus particles, or molecules, or organisms are in themselves either isotropic

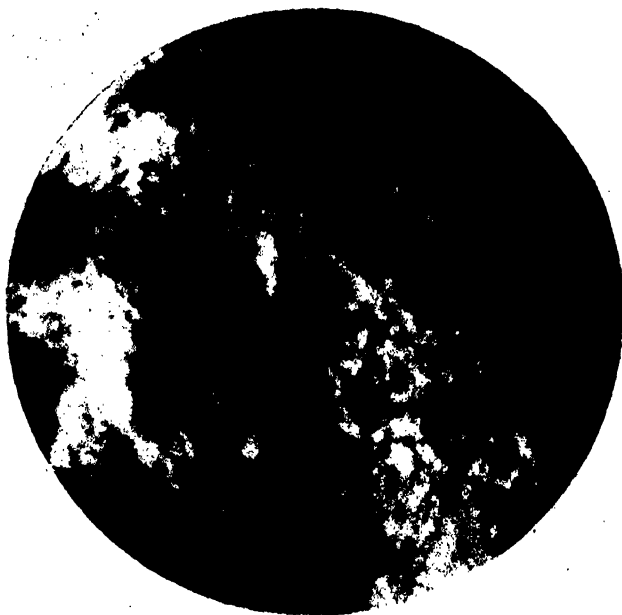


FIG. 6. Photomicrograph of droplet from the bottom layer (figure 4), taken with the aid of a polarizing microscope. $\times 135$. (Photograph by J. A. Carlile.)

or nearly so, demonstrates that they are not the analogs of those living organisms exhibiting permanent double refraction. Rather they must be considered the analogs of one of the components of living organisms showing paracrystallinity, for example, the nucleoproteins found in the sperm head.

SUMMARY

The solutions of tobacco mosaic virus protein exhibit many interesting colloidal optical properties. It has been known for some time that dilute aqueous solutions of the virus protein exhibit double refraction of flow (1, 8, 17). It has now been shown that, when dissolved in liquids having

a refractive index approaching that of the protein itself, little or no stream double refraction is obtained. Ultracentrifuged jelly-like pellets of the protein have properties characteristic of the liquid crystalline or paracrystalline state. As was shown by Bawden and Pirie (1) and confirmed in this laboratory (8), relatively concentrated solutions of the protein separate into two layers on standing, the bottom, more concentrated one being liquid crystalline. It was found in the present investigation that the Tyndall effect of the upper layer differs markedly from that of the lower layer. In the top layer the scattered light is depolarized to a small extent, whereas in the bottom layer the scattered light is very largely depolarized. All of these results are consistent with the conclusion that the tobacco mosaic virus protein particles or molecules are rod-shaped nucleoproteins having very little or no intrinsic double refraction. With respect to this latter property, the virus protein differs distinctly from the sperm cells of the cuttlefish and cells of other living organisms which have the property of double refraction or paracrystallinity.

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X-RAY DIFFRACTION STUDIES ON HEAVY-METAL FERROCYANIDE GELS¹

HARRY B. WEISER, W. O. MILLIGAN, AND J. B. BATES

Department of Chemistry, The Rice Institute, Houston, Texas

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Most heavy-metal ferrocyanides are so insoluble that they are thrown down in a highly gelatinous form on mixing even dilute solutions of metallic ion and ferrocyanide ion. The tendency of the gel to carry down ferrocyanide ion is so strong that the precipitation of the metal is incomplete on mixing equivalent amounts of metallic and ferrocyanide ions. This strong sorption is illustrated by the carrying down of potassium ferrocyanide, sodium ferrocyanide, and hydroferrocyanic acid during the precipitation of copper ferrocyanide (figure 1) (7, 11). Some of the heavy-metal ferrocyanide gels thrown down with excess ferrocyanide ion are assumed to be double salts such as $2\text{Cu}_2\text{Fe}(\text{CN})_6 \cdot \text{K}_4\text{Fe}(\text{CN})_6$. From the potassium ferrocyanide curve in figure 1, it might be argued that a definite double salt is formed having the formula $5\text{Cu}_2\text{Fe}(\text{CN})_6 \cdot 2\text{K}_4\text{Fe}(\text{CN})_6$, and that the upper portion of the curve represents the sorption of potassium ferrocyanide by the double salt. Although this is possible, the evidence is not sufficient to establish the existence of a definite double salt of this formula.

Attempts have been made to determine the composition of the precipitated ferrocyanide gels by electrometric (1, 8, 9) and conductometric (4, 5, 6) titration. The most recent work of this kind was done by Britton and Dodd (2), who made conductivity measurements at 25°C. on mixtures of heavy-metal salts and potassium ferrocyanide: first, in the form of direct conductometric titration of 125 cc. of 0.02 *M* salts with 0.1 *M* potassium ferrocyanide; and second, on similar mixtures of reactants which had stood in a thermostat until equilibrium was set up. In figure 2 are given the curves constructed from data corresponding to equilibrium conditions and the horizontal lines which represent the specific conductivity of potassium sulfate formed as a result of the equation:



¹ Presented at the Fifteenth Colloid Symposium, held at Cambridge, Massachusetts, June 9-11, 1938.

The values of $x [= K_4Fe(CN)_6]$ deduced from the conductivity data, and from analysis of the precipitates formed in the presence of varying excess of potassium ferrocyanide, are summarized in table 1 (Britton and Dodd). The direct analysis of the precipitates is of little use in estimating the exact composition, since they are peptized before they can be washed free from entrained salt. Hence the values in the last column of table 1 represent only very rough approximations.

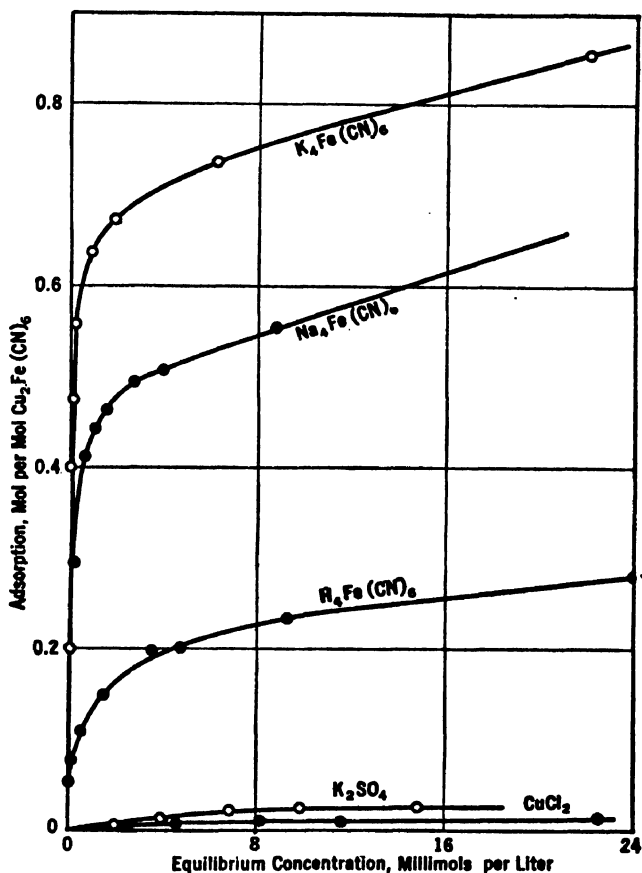


FIG. 1. Sorption of salts by copper ferrocyanide gel

Britton and Dodd recognize that the conductometric and analytical evidence given above is insufficient to decide whether the $M_2Fe(CN)_6$ - $K_4Fe(CN)_6$ mixtures are definite double salts or sorption complexes. Moreover, since any highly gelatinous double salt that may form will sorb ferrocyanide, it is not possible from conductometric data to deduce the ratio of $M_2Fe(CN)_6$ to $K_4Fe(CN)_6$ in the alleged double salts.

Since Milligan (10) found that the gel of copper ferrocyanide is crystalline to x-rays, it seemed likely that the ferrocyanide gels of other metals

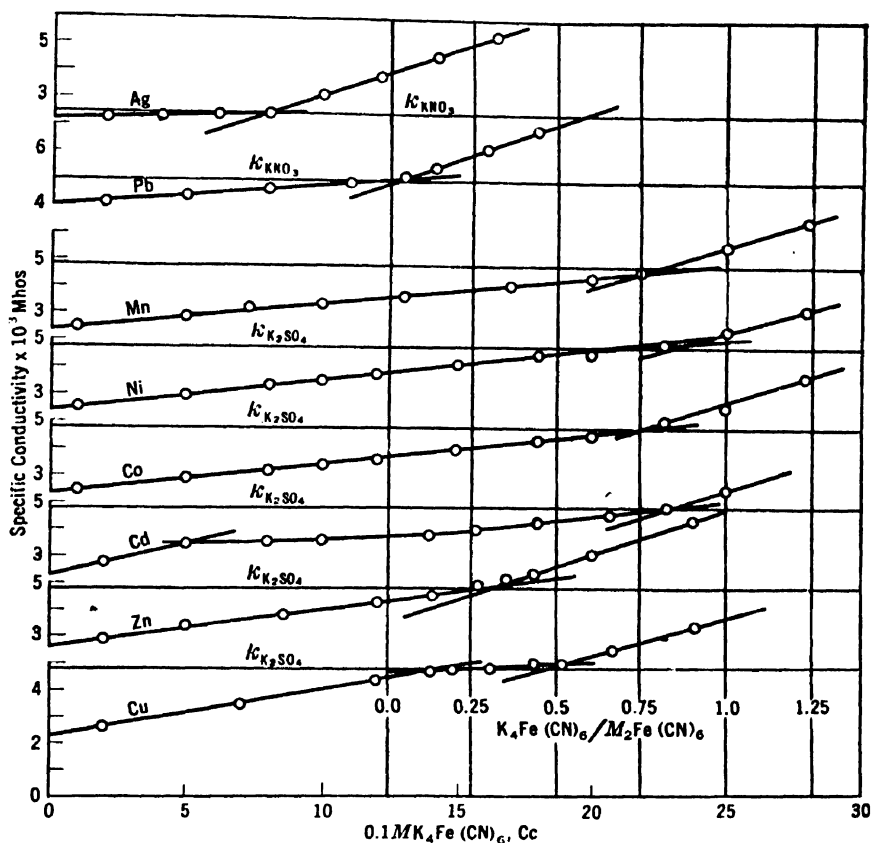


FIG. 2. Titration curves for ferrocyanide solution with various metallic salts (Britton and Dodd)

TABLE I

Potassium ferrocyanide in ferrocyanide gels

x = moles of $K_4Fe(CN)_6$ per mole of $M_2Fe(CN)_6$

M	FROM CONDUCTIVITY MEASUREMENTS				FROM DIRECT ANALYSIS <i>x</i>
	First break		Second break		
	0.1 M K ₄ Fe(CN) ₆	<i>x</i>	0.1 M K ₄ Fe(CN) ₆		
	cc.		cc.		
Cu.....	14	0.12	18.7	0.52	0.52 0.71
Zn.....			16.4	0.31	0.71 0.78
Cd.....			23.0	0.84	0.59 0.90
Co.....			22.3	0.78	0.50 0.74
Ni.....	19.7	0.58	23.4	0.87	0.56-1.22
Mn.....			23.0	0.84	0.83 0.92
Pb.....	12.5	0.0			Very small
Ag.....	8.3	0.33			0.33

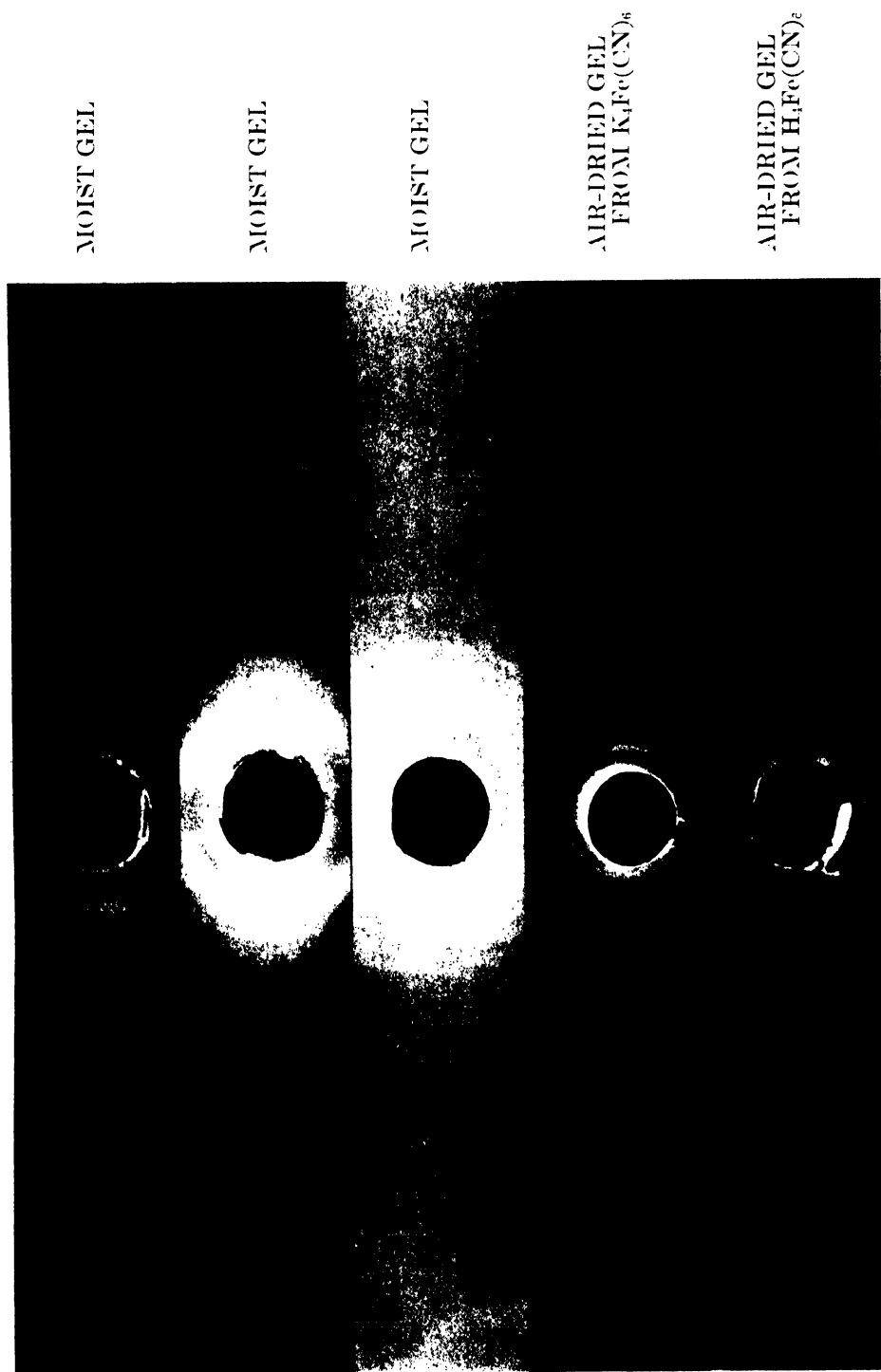


FIG. 3. X-ray diffraction patterns of copper ferrocyanide gels

would be crystalline. If so, the method of x-ray diffraction analysis should throw some light on the constitution of the gels formed under varying conditions. This paper gives a preliminary report of the results of the x-ray examination of the ferrocyanide gels of copper, cobalt, nickel, manganese, lead, zinc, cadmium, and silver.

EXPERIMENTAL

Copper ferrocyanide

In an investigation of the cause of the impermeability of the copper ferrocyanide membrane to ferrocyanide ion (11), it was concluded that the salt sorbs ferrocyanide ion strongly and irreversibly up to a composition of approximately 0.4 mole of potassium ferrocyanide per mole of copper ferrocyanide (figure 1). But, as already pointed out, the possibility of double salt formation can be neither proven nor ruled out by the results

TABLE 2
A series of copper ferrocyanide gels

SAMPLE NO.	SOLUTIONS MIXED					FINAL CON- CENTRATION OF CuCl_2	AMOUNT OF $\text{K}_4\text{Fe}(\text{CN})_6$ ADSORBED, MOLES PER MOLE OF $\text{Cu}_2\text{Fe}(\text{CN})_6$
	CuCl_2		$\text{K}_4\text{Fe}(\text{CN})_6$		H_2O		
	0.0874 <i>M</i>	0.0300 <i>M</i>	0.1173 <i>M</i>	0.0304 <i>M</i>			
	<i>cc.</i>	<i>cc.</i>	<i>cc.</i>	<i>cc.</i>	<i>cc.</i>	<i>millimoles</i>	<i>moles</i>
I	802.88		197.92		0	24.88	0.022
II		100.36		39.73	108.91	2.55	0.037
III		100.36		49.48	99.19	0.305	0.042
IV		100.36		54.50	94.17	0	0.117
V		100.36		59.34	89.33	0	0.224
VI		100.36		61.84	86.81	0	0.268
VII		100.36		64.36	84.31	0	0.319

recorded in figure 1. A series of gels was therefore prepared by mixing varying amounts of cupric chloride and potassium ferrocyanide as given in table 2. The gels were centrifuged and the supernatant liquids analyzed for copper and ferrocyanide. The copper determinations were made by the standard iodometric procedure, while the ferrocyanide analyses were carried out by titrating with standardized potassium permanganate. It will be observed that the first three samples in the table contain but little excess potassium ferrocyanide.

A duplicate of sample I was washed, using a centrifuge, until the last washing was free of copper and ferrocyanide ions. This gel was air-dried and analyzed by a method similar to that of Hartung (3). The dry gel was dissolved in 6 N sodium hydroxide, and boiled until copper oxide was precipitated. The filtered and washed copper oxide was dissolved in nitric acid, excess acid removed, and the copper determined as given above. The filtrate was neutralized and ferrocyanide determined by

titration with potassium permanganate. The sample was found to contain 41.53 per cent Cu, 24.42 per cent $\text{Fe}(\text{CN})_6$, and 34.05 per cent H_2O (by difference); the mole ratio $\text{Cu}/\text{Fe}(\text{CN})_6 = 1.962$.

The unwashed, moist gels obtained by centrifuging samples I to VII were placed in thin tubes of Lindemann glass for x-ray examination by means of the following procedure: The open end of the glass tube was thrust into a portion of the moist gel placed on a sheet of filter paper. The small quantity of gel obtained was moved toward the center of the glass tube by gentle suction, leaving about 4 to 5 mm. of empty tube below the

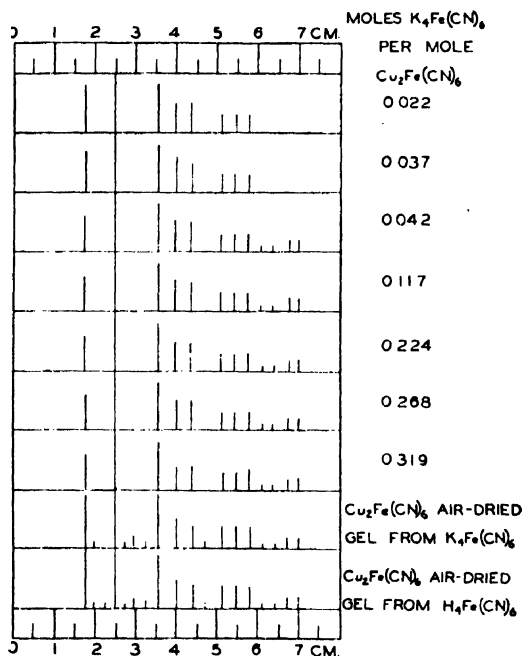


FIG. 4. Diagrams of the x-ray diffraction patterns of copper ferrocyanide gels containing varying amounts of sorbed potassium ferrocyanide.

gel. The Lindemann glass tube was then sealed off by means of a very small needle-point flame.

The various gel samples were examined by x-ray diffraction methods, using $\text{Cu K}\alpha$ x-radiation, in a camera 57.6 mm. in diameter, with an exposure time of 1 hr. The film was protected by aluminum foil from secondary radiation from the iron in the samples. Some typical patterns reproduced in figure 3 show the degree of crystallinity of the gels. The results with a series of gels of varying composition are represented diagrammatically in figure 4. For purposes of comparison the diagrams of practically pure copper ferrocyanide precipitated (a) with copper in excess and (b) with hydroferrocyanic acid in slight excess are included in the diagram. Since

the several patterns are identical within the limits of accuracy of the observations, it would appear that the ferrocyanide carried down by copper ferrocyanide gel is not combined to form a definite double salt. There are three possibilities: (1) that the excess ferrocyanide is adsorbed on the surface of the highly dispersed crystals, (2) that the excess ferrocyanide is dissolved in the normal salt without causing sufficient change in the diffraction pattern to be detected, and (3) that both adsorption and solid solution are involved in the process. Since the crystals are so minute, x-ray diffraction patterns of the gels are not sufficiently sharp to enable one to detect minor differences in position or intensity of the bands. Until further information is available it seems advisable to use McBain's term "sorption" in referring to the phenomenon, which may involve both adsorption and a small amount of solid solution.

Other ferrocyanides

To prepare the other ferrocyanide gels investigated, 125-cc. portions of 0.02 *M* solutions of the several salts were added to varying amounts of 0.1 *M* potassium ferrocyanide (cf. Britton and Dodd (2)). Each ferrocyanide was precipitated (1) with one-half the theoretical amount required to react with the metal, (2) with an amount corresponding approximately to the break in Britton and Dodd's titration curve, and (3) with three times the theoretical amount. The gels were thrown down with the centrifuge and the x-ray diffraction patterns obtained as described above for copper ferrocyanide.

The ferrocyanides of cobalt, nickel, and manganese. The x-ray diffraction patterns of the several gels precipitated under varying conditions are shown diagrammatically in figure 5. With all three salts the diffraction patterns of the gels are the same irrespective of the $K_4Fe(CN)_6 \cdot 2M_2SO_4$ ratio used in their preparation. This indicates that the potassium ferrocyanide carried down by the several gels is sorbed in an indefinite ratio and is not combined to give definite double salts. The breaks in the conductometric titration curves are therefore without significance in their relation to the possible formation of double salts. They may correspond approximately to the flat portion of the respective sorption isotherms.

A comparison of the diffraction patterns of the several ferrocyanides under consideration discloses that the positions of the lines are the same within the limits of the accuracy of measurement. The fairly sharp diffraction lines are in the same position, and the number and intensity of the lines are the same for the four salts, as nearly as can be estimated. This indicates that the salts are isomorphous, and have lattice constants that are nearly the same. This would be expected if the relatively large ferrocyanide anions were so arranged as to give spaces in which the smaller metallic ions are grouped. The fact that the ionic radii of the metallic ions under consideration are very nearly the same would account for

the apparently small variations in lattice constants among the several salts.

Lead ferrocyanide. The lead salt gives a precipitate composed of relatively large crystals with a low sorbing power. The diffraction pattern shown in figure 5 is different from that of the other salts in the same figure. This would be expected in view of the much larger ionic radius of lead ion. The low sorption capacity accounts for the break in the conductometric titration curve at a point only a little above that corresponding to equivalent amounts of lead and ferrocyanide ions.

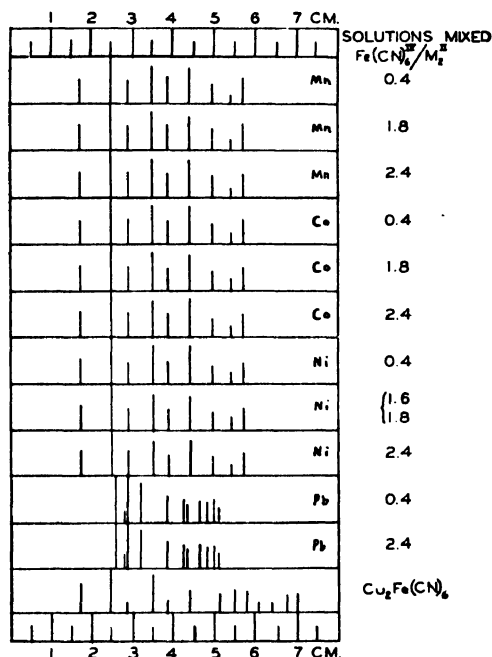
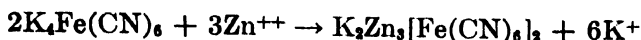


FIG. 5. Diagrams of the x-ray diffraction patterns of the ferrocyanide gels of cobalt, nickel, manganese, and lead.

The ferrocyanides of zinc, cadmium, and silver. The diffraction patterns of the ferrocyanides of zinc, cadmium, and silver are shown in diagrammatic form in figure 6. In contrast to the salts whose diffraction patterns are given in figure 5, the zinc, cadmium, and silver salts each give two patterns, depending on whether the gel is thrown down with metallic ion in excess or with ferrocyanide ion in excess. The two diffraction patterns for each of the three salts may correspond respectively to the normal salt and to a double salt with potassium ferrocyanide. It should be pointed out, however, that the possibility has not been excluded that the second pattern is due to a different crystalline modification or a different hydrate of the normal salt plus sorbed potassium ferrocyanide.

The composition of zinc ferrocyanide is of special importance, because

zinc may be estimated volumetrically by titration with potassium ferrocyanide in neutral or acid solution. The following reaction is said to take place



with the formation of a definite double salt. Referring to table 1 it will be seen that the observed equilibrium concentration of potassium ferrocyanide at the break in the curve is less than corresponds to the above formula, although in the rapid conductometric titration the break was observed at a point corresponding to the formula. This would seem to indicate that the precipitate is not a definite salt of the above composition, but is either zinc ferrocyanide with sorbed potassium ferrocyanide or a double salt containing less potassium ferrocyanide than the above, together with sorbed potassium ferrocyanide. To take care of possible variations

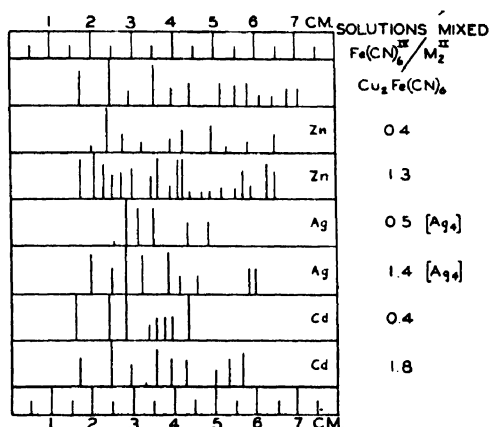


FIG. 6. Diagrams of the x-ray diffraction patterns of the ferrocyanide gels of zinc, cadmium, and silver.

in the composition of the precipitated gel and so to obtain accurate results in the estimation of zinc, it is essential not only that the conditions be rigidly controlled but also that they be exactly the same as in the standardization of the ferrocyanide solution against zinc.

Attention should be called to the fact that the diffraction pattern of the cadmium salt thrown down with ferrocyanide in excess is very similar to that of copper ferrocyanide. This suggests that the cadmium salt formed under these conditions is $\text{Cd}_2\text{Fe}(\text{CN})_6$.

SUMMARY

The results of this investigation may be summarized as follows:

1. The gels of the heavy-metal ferrocyanides carry down alkali ferrocyanides strongly. It is not possible to determine by conductometric or potentiometric titration whether the gels adsorb the alkali ferrocyanide or whether double salts are formed.

2. Since the heavy-metal ferrocyanides are crystalline to x-rays, x-ray diffraction analysis of the moist gels throws some light on the constitution of the gels formed under varying conditions.

3. Copper ferrocyanide precipitated in the presence of excess copper is practically pure $\text{Cu}_2\text{Fe}(\text{CN})_6$, which gives a distinctive x-radiogram. The gel thrown down with excess alkali ferrocyanide gives the same x-ray diffraction pattern as $\text{Cu}_2\text{Fe}(\text{CN})_6$ even when it contains as much as 0.3 to 0.4 mole of $\text{K}_4\text{Fe}(\text{CN})_6$ per mole of $\text{Cu}_2\text{Fe}(\text{CN})_6$.

4. The alkali ferrocyanide carried down by copper ferrocyanide gel is not combined to form definite double salts. The excess ferrocyanide is adsorbed, for the most part, on the surface of the highly dispersed crystals of copper ferrocyanide. The possibility that a small amount of alkali ferrocyanide is dissolved in copper ferrocyanide has not been excluded. The phenomenon is therefore referred to as sorption.

5. The ferrocyanides of copper, cobalt, nickel, and manganese, but not of lead, are isomorphous, with lattice constants that are nearly the same. The crystals of lead ferrocyanide are relatively large and have a relatively low adsorption capacity for ferrocyanide ion.

6. The ferrocyanides of zinc, cadmium, and silver each give two distinct x-ray diffraction patterns, depending on whether the gel is thrown down with metal in excess or with potassium ferrocyanide in excess. The two diffraction patterns for each of the three salts may correspond respectively to the normal salt and to a double salt with potassium ferrocyanide. The similarity of the diffraction pattern of the cadmium ferrocyanide gel, thrown down with ferrocyanide in excess, to that of copper ferrocyanide suggests that the cadmium salt formed under these conditions is $\text{Cd}_2\text{Fe}(\text{CN})_6$.

7. The breaks in the conductometric titration curves for metallic salts and alkali ferrocyanide are without significance in their relation to the possible formation of double salts. They may correspond approximately to the flat portion of the respective sorption isotherms.

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A NEW ASPECT OF THE COLLOIDAL GOLD REACTIONS¹

HANS M. CASSEL

Research Department, Colgate-Palmolive-Peet Company, Jersey City, New Jersey

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THE BASIC IDEA

There is a general agreement about the rôle of the ζ -potential as a stabilizing factor. The ζ -potential is a measure of the repelling forces between neighboring particles, hence a sufficient reduction in potential leads to coagulation. But this is not the only possible way of explaining the collapse of colloidal dispersions; there must be another principle.² If the attractive forces are sufficiently increased the repulsion will be overcome, with coagulation as the result. Such an effect, indeed, should be expected if a "colloidal agent" condenses in the capillary interspaces between the particles during their collision.

In figure 1a two spherical particles are shown in a given volume containing under pressure P a gas which is adsorbed on the surface of the particles. Now suppose the two particles to be brought in contact. Immediately (figure 1b) the pressure must decrease, owing to capillary condensation taking place between the particles. In the case of very strong adsorption forces the pressure may become almost imperceptible. To establish the initial state by separating the particles, an energy of activation is required which might well exceed by far the work afforded by the ζ -potential. To distinguish this type of coagulation from that occurring in the absence of hydrophilic colloids we shall hereafter speak of "agglutination."

This process, of course, involves the consumption of agglutinin. Accordingly, a minimum concentration must be surpassed to start agglutination. On the other hand, when the interspaces are completely filled (figure 2) the consumption will reach a maximum, the value of which, naturally, depends on the geometrical conditions for tightest pack-

¹ Presented at the Fifteenth Colloid Symposium, held at Cambridge, Massachusetts, June 9-11, 1938.

² This subject was comprehensively discussed at the Symposium on Hydrophobic Colloids, held by the Nederlandsche Chemische Vereeniging at Utrecht, November, 1937. The contribution of F. Th. G. Overbeck dealt especially with the present problem. (Nordemann Publishing Co., New York (1938)).

ing. Thus it may appear as if a chemical compound of stoichiometric proportions had been formed. If the concentration is further increased, not agglutination but protection may result. This would require the vapor pressure of the single particle film to be smaller than that of coupled particles (see figure 3).

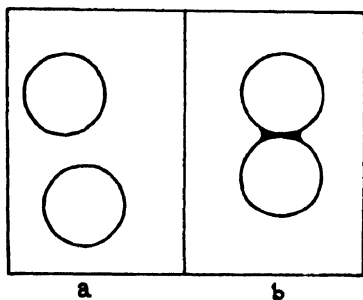


FIG. 1

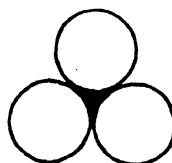


FIG. 2

FIG. 1. (a) Two spherical particles in a given volume containing under pressure P a gas which is adsorbed on the surface of the particles. (b) The two particles in contact; $p < P$.

FIG. 2. Apparent equivalence ratio = tightest packing

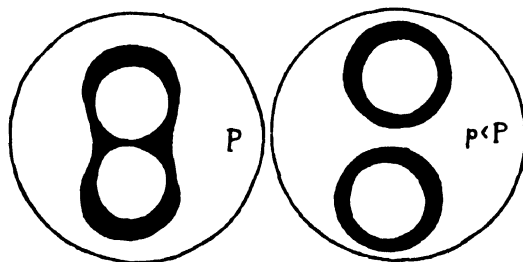


FIG. 3. Emulsification

DEVELOPMENT OF QUANTITATIVE RELATIONS

To define the conditions of capillary condensation, the relationship between the curvature of the adsorbing surfaces and the vapor pressures of the adsorbed films must be known. In the case of pure liquids the vapor pressure of smaller droplets is higher than that of larger ones. The contrary holds for concave menisci, according to the well known Gibbs-Thomson formula. However, we wish to know the vapor pressure of *films* adsorbed on curved surfaces.

Let us suppose that the film surrounding a spherical particle has, accidentally, the same vapor pressure as the adsorbent. Should we not expect the vapor pressure of the film to be exactly the same function of the curvature as that of the droplet? The thermodynamic treatment on the basis

of Gibbs' Theory of Capillarity (3) confirms this expectation and leads to the conclusion (2) that the vapor pressure (thermodynamic potential) of the film-forming substance, for a given value of the interfacial density, Γ , either increases or decreases with increasing curvature. The decision as to what will happen depends on the sign of the term $\frac{\sigma}{2\Gamma/r - c}$, where σ is the interfacial tension, r the radius of the interface, and c is the concentration of the film substance in solution (mass per unit volume). When $2\Gamma > rc$ we have to deal with a tendency toward condensation in concavities, hence agglutination can be expected. On the other hand, when $2\Gamma < rc$ the tendency is to condense preferentially upon convex interfaces of smaller radii. Hence, emulsification and protection should be possible.

As shown in a previous publication this theory agrees with experiences in emulsification. Nothing seems to be in the way of applying this view to the reactions of hydrophilic sols with hydrophobic suspensoids in general, disregarding for a first approximation departures from the spherical symmetry of crystalline particles.

COMPARISON WITH EXPERIMENTAL FACTS

From the present standpoint the whole behavior of hydrophilic sols toward gold sols depends entirely on the individual shape of the adsorption isotherm. Unfortunately, not a single isotherm is known as yet, either on plane or on curved surfaces. Thus we have to make conjectures according to the known facts which consist chiefly in agglutination numbers (minimum amounts to produce "sensitization") and in protection numbers (minimum amounts to inhibit agglutination). In not a single case have the actual concentrations been determined!

Figure 4 shows two hypothetical adsorption isotherms drawn in a Γ - c diagram and representing the adsorption on a particle of radius r . The whole field is divided into two fields by the straight line $2\Gamma = rc$. Those parts of the isotherms rising above this discriminant line define a zone of possible agglutination, while those parts lying beneath the discriminant, where $2\Gamma < rc$, outline a zone of possible protection.

We read from the diagram that agglutination can occur at much lower concentrations than protection, which is in agreement with experiment. Furthermore, it becomes clear that no protection at all can be provided in case the adsorption is too strong (figure 5).

The addition of electrolyte will either increase or decrease the adsorption. The first, as a pre-stage of salting-out, seems generally to be the case in the determination of Zsigmondy's gold numbers. These conditions are supposed to be represented by the higher adsorption isotherm in figure 4. Here we see the protection zone for the particle size r consider-

ably reduced. However, protection remains possible for larger sized particles, as illustrated by the discriminant r' having a steeper slope than r . This is the way the theory accounts for the characteristic feature of the gold sol reactions with hydrophilic sols, in that the disturbance of stability through electrolytes does not induce complete precipitation but ends in reestablishing stable conditions for larger aggregates, in spite of the strong electrolytes present.

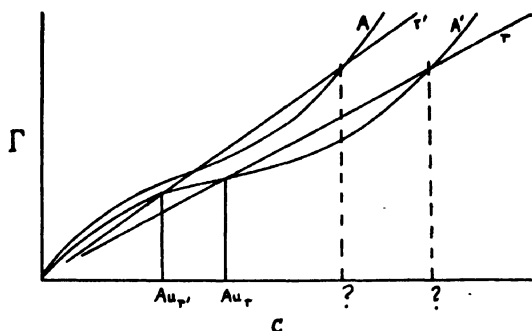


FIG. 4. The adsorption on a particle of radius r is shown in the presence and in the absence of electrolyte by curves A' and A , respectively. The straight lines r and r' represent the discriminants for particles of radii r and $r' > r$. Au_r and $Au_{r'}$ indicate the corresponding gold number concentrations. The question marks indicate "upper gold numbers."

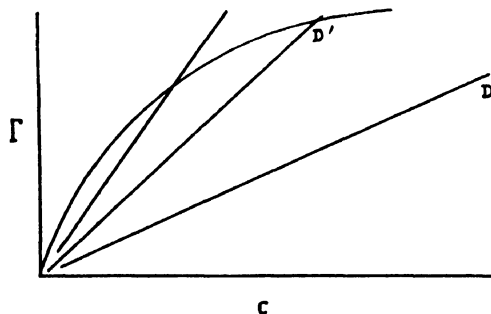


FIG. 5. This figure exemplifies strong adsorption where the discriminants even of rather large particles lie beneath the isotherm.

Zsigmondy's definition of the gold number implies the assumption that protection should always be enhanced by increasing the concentration of the colloids. However, while the chief concern has been to find out the best conditions for well-defined color changes, in actual practice this supposition has often been omitted. In violation of the original definition many so-called gold numbers were determined by the minimum amount of substance required to *produce* color changes instead of by those required to *prevent* them!

In any case caution is advisable in interpreting the presumably characteristic figures available in the literature, which may represent either the lower or the upper limit of the stability zone without apparent discrimination. Thus, for albumin, gum arabic, sodium oleate, and sodium laurate "upper gold numbers" are reported, as involuntarily demonstrated by the statement of Zsigmondy and Thiessen (4) that certain substances even at rather high concentrations do not effect any color changes, either spontaneously or on the addition of sodium chloride. These substances are those just mentioned!

From the present point of view such a behavior of hydrophilic sols can be foreseen. As already emphasized, the specificity of their reaction depends entirely on the shape of the adsorption isotherm. Let us imagine a type of curve which, up to rather high concentrations, always lies below the discriminant of the particle size chosen. Consequently, according to the theory, neither agglutination nor sensitization can be expected in the whole range of concentration limited by the "upper gold number." As a matter of fact, the gold numbers of the last-mentioned substances are representative of the higher values in Zsigmondy's classification.

There is one more argument in favor of the present view. If the low gold numbers correspond to the lower stability limit and the higher values to the upper limit they should be differently affected by changes in the size of the particles. It follows from the diagram (figure 4) that for discriminants of larger particles the protection zone is widened towards lower concentrations at the lower limit, but the opposite holds at the upper limit. Herewith it agrees that the gold numbers of soaps, dextrin, and albumin, which we recognized as "upper gold numbers," increase with increasing particle size, whereas the lower class colloids behave diametrically differently.

No one seems to have realized the possibility of gold numbers in the wider sense of the word, with the remarkable exception of such a critical observer as Wilhelm Biltz (1) who, studying the colloidal properties of dextrans, stated as early as in 1913 that two and more gold numbers may occur in different concentration ranges of the same substance.

So far as I can see, no contradictions are known to the present attempt to gain a unitarian aspect of the reactions between hydrophobic colloids and hydrophilic substances.

The results seem to encourage further experimental checking of the theory. If the present view is correct it should be promising to consider the behavior of gold sols as a prototype for certain antigen-antibody reactions.

In closing I wish to express my gratitude to Mr. Robert B. Colgate, Chairman of the Industrial Research Council, for his part in making this paper possible.

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STUDIES ON GELATION AND FILM FORMATION OF COLLOIDAL CLAYS. I¹

E. A. HAUSER AND D. S. LE BEAU²

*Department of Chemical Engineering, Massachusetts Institute of Technology,
Cambridge, Massachusetts*

Received July 1, 1938

The mechanism which leads to the formation of gels is still a matter of considerable controversy. A critical review of the literature leaves the impression that the lack of a satisfactory and general explanation for this so common and important phenomenon lies not so much in its admitted complexity but in the fact that so far sufficient attention has not been paid to the gelation of simple systems, i.e., systems whose components are well defined and which permit actual observation of the changes which the system undergoes in its transition from sol to gel. Most of the theories are based on assumptions only, or are derived by indirect deductions.

For instance, the gelation of a gelatin sol upon cooling, or of rubber solutions in the presence of sulfur and accelerators, etc, is assumed to be the result of a felting together of long-chain molecules (8) and the formation of bridges and cross linkages between them. The solvent is held mechanically in the network formed or part of it may be immobilized by solvation.

The formation of silica gels is considered also today as the result of a chain-like arrangement of neighboring silicic acid molecules by condensation (splitting off of water) (6).

These assumptions have been so generally accepted that even the gelation of systems with microscopically or ultramicroscopically discernible particles has been considered to be caused primarily by a chain-like or pearl-string-like aggregation of these particles (10).

In the case of soap gels we frequently find a string-like aggregation of the highly disperse soap micelles on cooling the soap stock. However, such an arrangement cannot be essential for the gelation of soap, since gels can also be obtained without any such alignment and felting.

Although it cannot be denied that gelation is facilitated in many cases where the disperse phase consists of organic molecules joined, by primary

¹ Presented at the Fifteenth Colloid Symposium, held at Cambridge, Massachusetts, June 9-11, 1938.

² Present address: Dewey & Almy Chemical Co., Cambridge, Massachusetts.

valences, in chains of high molecular weight, or where condensation leads to chain-like aggregates, we have ample evidence that such a structure is not essential for an explanation of all types of gelation.

Extremely dilute and monodisperse colloidal clay sols³ are excellent examples to disprove this general theory.

As a result of previous work pertaining to the production of monodisperse fractions of colloidal clays ranging in apparent average particle diameter from 14 to 180 m μ (5), it was found that the concentration of clay necessary to obtain a gel (system exhibiting yield point) decreases with decreasing particle size, and that gels with extremely low concentration (< 0.1 per cent) of the disperse phase could be produced with the smallest particle size fractions. Very careful systematic ultramicroscopic studies of *freshly* prepared gels of concentrations not exceeding 0.1 per cent did not permit, contrary to previous assumptions, the detection of any ultramicroscopically visible specific alignment or grouping of the disperse phase. Results reported previously where grouping of particles had been observed were caused by excessive addition of electrolyte.

However, there might remain the possibility that invisible particles form the "missing links." Therefore a carefully prepared fraction of medium particle size, i.e., one from which all smaller particles had been carefully removed by repeated supercentrifugal fractionation, was selected for the present investigation to guarantee the absence of smaller, possibly undetectable particles. If such a fraction was studied in a slit-ultramicroscope (using an air-tight chamber), the particles were present in vivid Brownian motion. However, contrary to older observations carried out with unfractionated, or insufficiently fractionated, sols, only faint twinkling could be observed. This indicates that the particles in the selected fraction and concentration used are not excessively anisometric. This confirms the prevailing concept of the shape of the individual clay particle as deduced from x-ray diffraction analysis.

It is assumed that such a particle consists of layers of silicon and aluminum (the latter being replaceable by magnesium) bonded together by oxygen. Whereas the length and width of these sheets do not vary with the water content, the thickness shows very pronounced changes (1). There exists ample evidence that the difference in observed apparent particle sizes is due primarily to a different number of such layer units stacked up on each other and to a far smaller degree to any difference in the length or width of the atom sheets themselves.

Upon adding electrolyte to such a dilute fractionated sol, one observes a decrease in displacement of the particles due to Brownian motion, without being able to detect any alignment, grouping, or any specific structure. Upon reaching a certain concentration of electrolyte in the system, Brown-

³ The term "colloidal clay" as used in this paper refers to montmorillonite, if not otherwise specifically stated.

ian motion ceases entirely. The individual particles may occasionally still show some rotation, but even so they remain fixed in their position (figure 1). At this stage the viscosity of the system has increased to a point where air bubbles do not rise any more. However, the slightest mechanical disturbance will immediately result in a revival of Brownian motion, which again comes to a standstill as soon as the outside influence stops (a *truly* thixotropic gel). Even if we assume that not all particles are visible when the system comes to a standstill—some might lie with their thinnest axis parallel to the direction of illumination—it seems highly improbable that all the optical voids should be filled with such invisible particles; moreover, such a configuration would have to be detectable by changing the azimuth. However, this is not the case.

It is theoretically impossible to determine the actual distance between reflection disks in an ultramicroscope. The only experimental statement which can be made is that the individual visible reflection disks are separated and that when a very narrow slit is used the probability that particles which do not happen to be in focus join the sharp reflection disks is negligible.

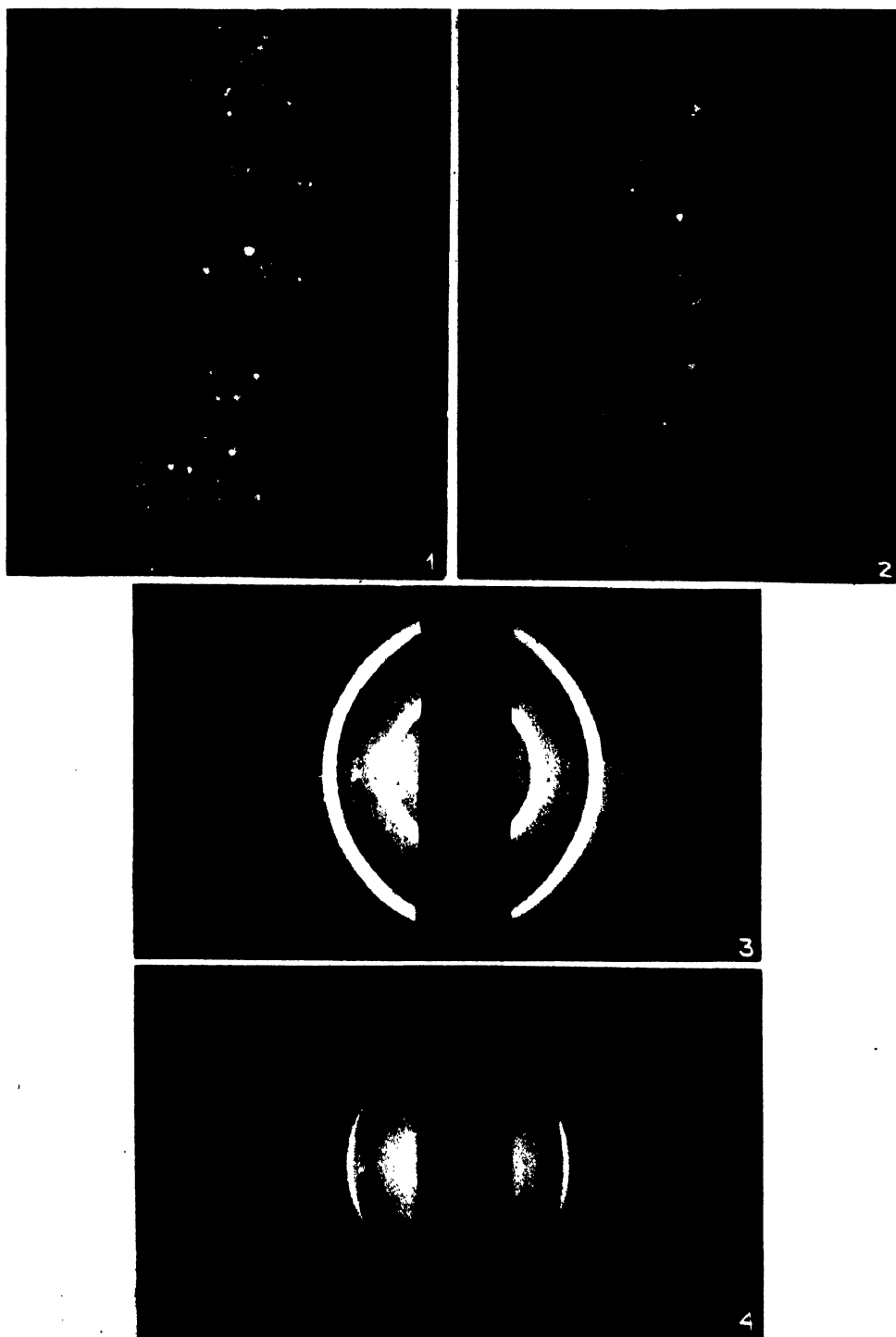
The disks might be caused by a group of primary particles, which is to be doubted. But even then such hypothetical groups would be separated from each other and exhibit no coherent structure, as postulated, for example, by the mechanical theory (7). This theory assumes that the individual particles actually touch each other in random arrangement, forming a skeleton comparable to a house of cards.

If only a slight excess of electrolyte is added, one observes the formation of "ultraflocks"⁴ separated by narrow channels (figure 2). Although such a system will generally still be considered as a gel, and will not yet exhibit immediate syneresis, it is unquestionably present in a state of incipient coagulation. Further addition of electrolyte results in the formation of microscopic—and, finally, macroscopic—flocks. A *gel-like* system will persist as long as the flocks are sufficiently loose in structure, of microscopic size, and coherent. However, the above experiment demonstrates that *true gelation* is present prior to any sign of flocculation or agglomeration.

It is beyond the scope of this paper to discuss these experimental facts from a theoretical angle, yet it might be pointed out that we consider the formation of these gels to be caused by the particles taking up equilibrium positions in relation to each other. Since the overall attraction⁵ between

⁴ The term "ultraflock" should denote flocculation, which is visible only in the ultramicroscope.

⁵ For the present discussion it is irrelevant if one considers only the disperse phase responsible for the development of these forces, or, in accordance with Wo. Ostwald (9), attaches at least equal importance to the composition of the dispersion medium and its ionic arrangement. A detailed theoretical discussion of these pertinent problems is in preparation.



FIGS. 1-4

identical particles of equal size and shape in a given suspension must be considered as constant for every time differential and of sufficient magnitude in the colloidal range to cause permanent cohesion of the solid phase, if not counteracted by a repulsion force, it is the latter which becomes of predominant importance. Repulsion is composed of various factors, as, for example, the electric charge of the particle, the composition and nature of the ion arrangement in the dispersion medium, lyosorption or solvation, etc. Equilibrium will be reached as soon as the overall attraction is compensated by overall repulsion. That such a system exhibits a yield point finds its simple explanation in the fact that work must be done to move a particle out of its equilibrium position, i.e., to overcome the repelling force of the neighboring particles as well as their attraction, because of which they try to hold the particle in place. This theory is at variance with recent deductions based on the additive character of the London-van der Waals forces (4). The present theory considers repulsion as predominant, whereas the latter stresses the importance of attraction forces.

That dilute gels of hydrated clays like montmorillonite are not the result of any preferred structure or orientation is also demonstrated by a complete lack of alignment and the absence of tactoids or the like. On the contrary, the sols show orientation in polarized light only when in motion, but neither the sol at rest nor the gel is doubly refractive. On the basis of such a concept gelation must become more pronounced, the smaller the particles, because a system of a given volume can be considered the more volume-dispersed the more particles are available. Maximum gelation will exist if the particles are of uniform size and uniformly spaced (a system of random orientation but great regularity of distribution).

Still more striking is the evidence offered by the changes such gels undergo upon further drying. For example, if a sol is first converted into a gel by evaporation and the gel is spread on an appropriate support or deposited thereon directly from the sol state by centrifugal action, and then allowed to dry out completely, we observe with the aid of vertical dark-field illumination that the particles when forced closer together line up or actually snap into their new location, forming long, interlacing filaments or fiber bundles. The presence of separate reflection disks, as ob-

FIG. 1. Gel prepared from montmorillonite. Exposure time = 30 sec. Note the sharpness of the reflection disks. $\times 500$.

FIG. 2. Ultraflocks formed upon the addition of a slight excess of electrolyte. $\times 500$.

FIG. 3. X-ray of a film formed by drying the gel. Direction of x-rays vertical to the plane of the film.

FIG. 4. X-ray of a film formed by drying the gel. Direction of x-rays parallel to the plane of the film.

served in the sol and gel stage, gives way to continuous thread-like aggregations, which upon continued evaporation seemingly grow into larger crystals of highly anisometric shape. These filaments interweave and tie together by tridimensional cross-linkages, resulting in a coherent network or structure. *After complete desiccation an absolutely self-supporting film is obtained, which can be easily removed from its support as a coherent sheet.*

Such film production can be made absolutely continuous, starting with an appropriate sol by using the right type of filming machine. Another conceivable possibility is the production of fine threads by a combination spinning-drying process. Similar results have also been obtained with other clay minerals, vanadium pentoxide sols, etc. Depending on the particle size fractions used, films of varying degree of brittleness and flexibility are obtainable, the latter increasing with decreasing particle size. X-ray diagrams of such films,⁶ taken vertical and parallel to its plane, reveal a typical Debye-Scherrer montmorillonite pattern in the former case, and a clear fiber pattern in the latter. This simply proves that all the particles have arranged themselves with the same crystallographic axis, parallel to the support (3) (figures 3 and 4).

The formed crystal threads are slightly doubly refractive.

The possibility of producing extremely thin, coherent, and self-supporting films without any binder and of high purity of the material offers a new method of studying the infrared absorption spectra of montmorillonite and other filming substances. Since these films can be produced from Na^+ , Ca^{++} , or H^+ , or any other adsorbed cation, further investigation should prove of great interest as to lattice configuration and especially water adsorption and absorption. So far distinct absorption bands have been observed at a reciprocal wave length of 3700 cm.^{-1} due to free hydroxyl groups and between $3600\text{--}3200 \text{ cm.}^{-1}$ due to associated hydroxyl groups or adsorbed water. Whereas increasing temperature of drying the films reduces the second absorption band, the first remains practically unchanged⁷ (2).

Films prepared from sodium bentonite swell and finally go into solution, if placed in water, whereas films of hydrogen bentonite resist very markedly and only show limited swelling. If sodium bentonite films are heated to white heat, they become water-resistant and decidedly stronger, the flexibility decreases, and they closely resemble mica in appearance and properties. If the films are subjected to high pressure they become transparent and much stronger. The translucency of the original film increases

⁶ The x-ray diagrams were kindly taken by Professor B. E. Warren of the Department of Physics, Massachusetts Institute of Technology.

⁷ Dr. Bowling Barnes of the American Cyanamid Co. was so kind as to determine the infrared absorption spectra.

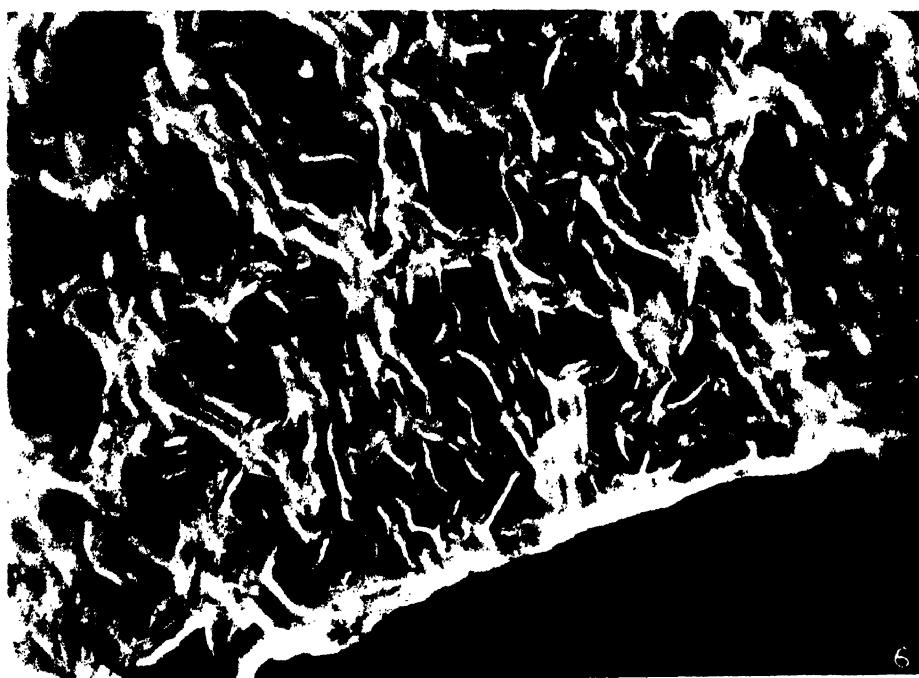
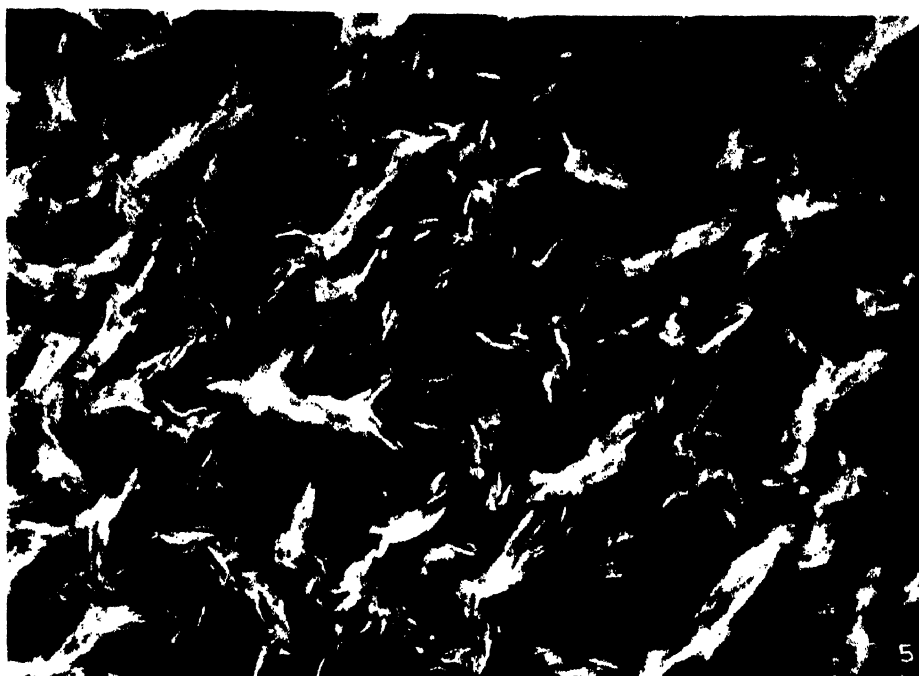


FIG. 5. Formation of crystal fiber bundles
 FIG. 6. Structure after complete air-drying

with decreasing particle size and depends to some extent on the raw material used (aluminum silicate, magnesium silicate, iron content, etc.).

The structures which have been so far observed with dark-field microscopy are so numerous and complex that it has been impossible as yet to draw definite conclusions as to their significance for the formation of the film. However, it seems clear that high temperatures and pressure cause a drastic change in the basic crystal structure of the film (figures 5, 6, and 7).

The authors wish to have it understood that the discussion of the formation of self-supporting clay films is to be considered only as a brief sum-



FIG. 7. Crystal formation after heating above 450°C.

mary of preliminary observations. A more detailed report will be published at a later date. The ability of inorganic particles to align and grow together to form the discussed networks or structures excludes the pre-existence of a preferred arrangement in the gel. Even the slightest agglomeration in the gel, resulting in vacuolae, prevents the formation of continuous films. Furthermore, this phenomenon seems to offer a new insight into the possibility of crystal growth from colloidal dispersions instead of from true solutions and might be of special value for mineralogical and geological considerations. The work is being continued.

In conclusion we should like to mention a peculiar phenomenon which

was observed in the very finest fractions of bentonite. Besides the particles exhibiting regular Brownian motion, there exist particles which travel through the field of vision in a straight-line motion, like shooting stars, and then suddenly disappear. All tests⁸ for living organisms (bacteria) were absolutely negative. At present the only plausible explanation for this peculiar phenomenon seems to be the possibility of point disintegration of submicrons, i.e., crystals, resulting in a recoil type of motion.⁹ Further work is in progress.

SUMMARY

The most commonly accepted theories of gelation are discussed in connection with ultramicroscopic studies of the gelation of extremely dilute colloidal clay sols. A new concept for the transition from sol to gel is offered.

The formation of self-supporting coherent pure colloidal clay films of high flexibility has been observed, and the arrangement of the individual particles in chain aggregates is demonstrated. The possibility of crystal growth from colloidal dispersions and not from true solutions is considered.

X-ray and infrared absorption diagrams are discussed.

Attention is drawn to a peculiar rocket-like movement of particles found only in the finest colloidal clay fractions.

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⁸ These tests were kindly carried out by Dr. M. W. Jennison of the Department of Biology, Massachusetts Institute of Technology.

⁹ This suggestion was originally made by Dr. M. J. Buerger of the Department of Geology, Massachusetts Institute of Technology.

COMMUNICATIONS TO THE EDITOR

THE SOLUBILITY OF CALCIUM BICARBONATE¹

The idea that passing carbon dioxide into a suspension of calcium carbonate solubilizes part of the salt as soluble calcium bicarbonate is so plausible that no one seems ever to have questioned it. Professor Bancroft reports that he can find no account of an experiment performed to determine whether calcium bicarbonate is in true solution. The point seemed worth considering, because there are natural streams of water which are green (apparently a structural green), yet every ordinary source of the color seems to be ruled out. If calcium bicarbonate were in colloidal suspension, this fact might account for the color.

Actually, there are three, not two, possible cases in this problem: (1) carbon dioxide might peptize calcium carbonate as such; (2) carbon dioxide might form calcium bicarbonate as a colloidal suspension; (3) carbon dioxide might form calcium bicarbonate in true solution. Accordingly, the following experiment in ultrafiltration was carried out.

Carbon dioxide was bubbled through a solution of c.p. calcium hydroxide for several hours. A collodion bag, previously tested for soundness with a Congo red sol, was filled with a portion of the suspension containing 26.8 mg. of calcium, calculated as calcium hydroxide, and immersed in distilled water. After standing overnight, the diffusate and the residue in the bag were analyzed for calcium by titration with hydrochloric acid. Any soluble calcium impurities in the original hydroxide would not interfere in this procedure; moreover, these were negligible in amount. The residue contained 6.2 mg., again calculated as calcium hydroxide, and the diffusate, 20.4 mg. This accounts for 26.6 mg., which differs negligibly from the amount introduced into the bag. The calcium which did not diffuse through seemed to be all in the form of calcium carbonate, since a precipitate settled to the bottom of the bag during the experiment.

The diffusate was examined with a Tyndall beam in direct comparison with an identical tube containing freshly drawn distilled water. The diffusate was optically empty, which made examination with an ultramicroscope unnecessary. Professor Mason of the microscopy staff supervised this examination.

Evaporation of a portion of the diffusate gave a residue which effervesced upon treatment with hydrochloric acid. The diffusate remained clear for several hours after the experiment, when it was discarded.

¹ Received June 13, 1938.

The diffusion experiment was repeated with bags which were dried for a longer time after preparation than the first one before being wetted, and which were soaked in distilled water a shorter time before use. (The first bag was dried for 10 min. and soaked for 12 hr.) This procedure should give smaller pores than the shorter drying period and/or a longer soaking period. Again the calcium diffused through the collodion membrane.

The conclusion is drawn that carbon dioxide converts the major portion of the calcium carbonate precipitated from a solution of calcium hydroxide into calcium bicarbonate, which is in true solution. Very reasonably, people have believed this all along, but it is satisfying to have experimental evidence to support the belief.

STEPHEN S. HUBARD.

Department of Chemistry
Cornell University
Ithaca, New York

THE STANDARD BATTERY (A CORRECTION)¹

R. B. Elliott and G. A. Hulett in a previous article (J. Phys. Chem. **37**, 489 (1933)) have described the characteristics of standard batteries, but we find that the specifications given do not give a satisfactory electrolyte. The constancy of current and voltage of these batteries depends on maintaining the electrolyte within quite narrow limits. For the combination $\text{Cd}_{\text{amg.}}|\text{CdSO}_4 \text{ solution} \text{ Hg}_2\text{SO}_4|\text{Hg}$, Weston (U. S. patent 494,824, April, 1891) found that a cadmium sulfate ($\text{CdSO}_4 \cdot 8/3\text{H}_2\text{O}$) solution, saturated at 4°C., was satisfactory. This combination has a practically zero temperature coefficient of E.M.F. for all ordinary temperatures and furnishes a most satisfactory working standard of E.M.F. It is not an easy matter to make a saturated solution at 4°C., especially with $\text{CdSO}_4 \cdot 8/3\text{H}_2\text{O}$, which has an extraordinarily slow rate of solution. Solubility data show that a solution of $\text{CdSO}_4 \cdot 8/3\text{H}_2\text{O}$ saturated at 4°C. is 43.18 per cent CdSO_4 and 56.82 per cent H_2O , so that 100 g. or 100 cc. of water dissolves 112.75 g. of $\text{CdSO}_4 \cdot 8/3\text{H}_2\text{O}$. For the 30-cm. battery described (J. Phys. Chem. **37**, 492 (1933)) one needs 4 liters of water and 4.5 kg. of $\text{CdSO}_4 \cdot 8/3\text{H}_2\text{O}$. The best grade of commercial sulfate, or the cloudy crystals left over from recrystallizing the salt, are entirely satisfactory. Several hours stirring will be necessary to effect solution. Heating above 70°C. is not desirable. Four liters of water and 4.5 kg. of $\text{CdSO}_4 \cdot 8/3\text{H}_2\text{O}$ will give 5.3 liters of solution, and to this is added 25 cc. of c.p. sulfuric acid (density 1.84). This will give an acidity of 0.085 molar sulfuric acid,

¹ Received April 18, 1938.

which satisfactorily prevents hydrolysis of the mercurous sulfate and makes the cathode system a reversible equilibrium system.

The remaining specifications (J. Phys. Chem. **37**, 492 (1933)) are quite satisfactory. It may be well to append specifications for a battery made up in a 20-cm. diameter crystallizing dish. Such a battery will deliver 3 milliamperes without variations of more than 1.5 parts in a million, and two such batteries in series are quite satisfactory on a high-resistance potentiometer circuit. A 20-cm. crystallizing dish or flat-bottomed cylinder is satisfactory. The bottom of the dish is covered with mercury to a depth of about 5 mm., some 2 kg. being sufficient. The best grade of mercury is satisfactory, or used mercury may be shaken in a separatory funnel with 1:10 sulfuric acid (1.6 molar) and an excess of mercurous sulfate. Above this layer of mercury one adds the 2.6 liters of electrolyte made up by dissolving 2250 g. of a good grade of $\text{CdSO}_4 \cdot 8/3\text{H}_2\text{O}$ in 2 liters of water and adding 15 cc. of c.p. sulfuric acid (density 1.84). This gives a depth of some 8.5 cm. of electrolyte. The mercurous sulfate depolarizer is easily prepared chemically in a suitable flask or beaker by adding 50 cc. of sulfuric acid (density 1.84) to 500 cc. of water and in this dissolving 200 g. of c.p. mercuric sulfate. Sulfur dioxide is passed through this solution until the mercuric sulfate is reduced and the precipitate of mercurous sulfate begins to turn gray, owing to finely divided mercury. To this system one may add some mercury and stir overnight on a water bath to eliminate the very finely divided mercury due to surface tension effects and also to recrystallize some of the mercurous sulfate. This product is brought into a Büchner funnel, the acid is removed by filtration, and then the solid is washed twice with a minimum of the electrolyte. The cake of sulfate is freed from the filter paper and brought onto the mercury electrode in the electrolyte, where a uniform layer is easily obtained.

The cadmium amalgam anode should be about twice the area of the cathode and may be put into Petri dishes. It is prepared by melting together 110 g. of c.p. cadmium and 1000 g. of mercury; this is poured in equal portions into three 16-cm. Petri dishes. From a glass rod is made a low form of tripod that will hold a Petri dish about 1 cm. above the cathode; on this, separated by a glass triangle, the second Petri dish is placed, and the third on top of this. By suitably protected wires all three of these amalgams are connected with an anode binding post. This gives a total anode area of 603 cm^2 , which is quite satisfactory with the 314 cm^2 cathode. The battery must be covered to prevent evaporation from the electrolyte; a glass plate is used and, if necessary, some vaseline.

The above unit is a satisfactory one and may be built up in series or parallel to meet any requirement. It will give a constancy of E.M.F.

or current quite unapproachable by any other combination. When not delivering a current it gives a most satisfactory working standard of E.M.F., but must be calibrated like any Weston cell.

G. A. HULETT.

Department of Chemistry
Princeton University
Princeton, New Jersey

CORRECTION

In the article entitled "Decomposition and Synthesis of Hydrogen Iodide by Alpha Particles" (J. Phys. Chem. **42**, 617 (1938)) the exponent $\frac{4}{3}$ in equation 4, page 624, should be $\frac{1}{3}$.

KEREN GILMORE BRATTAIN.

NEW BOOKS

Organic Chemistry. An Advanced Treatise. Vols. I and II. By HENRY GILMAN, *Editor-in-Chief*. 1890 pp. New York City: John Wiley and Sons, Inc., 1938. Price: \$15.00 (complete).

This treatise has been prepared under the editorship of a board composed of Roger Adams, Homer Adkins, Hans Clarke, Carl Marvel, Frank Whitmore, and Henry Gilman, *Editor-in-Chief*. In addition, twenty-two contributors have shared in this undertaking.

The following sentences, taken from the preface, will make clear the general plan of this treatise. "There is a need for a general treatise of organic chemistry suitable for instruction at the graduate level. Such a book must focus attention upon new developments. At best, it can but serve the purpose of the moment and provide a point of departure for unceasing revision. The idea of a collaborative work by specialists in the several branches of the science was developed in 1934. Each author was asked to prepare a chapter dealing with a subject of particular interest to himself. It was hoped to obtain, in this way, an authoritative treatise which would cover most of the important phases of organic chemistry. . . ." "It is planned to revise both volumes at intervals, not only in order to bring the present material up to date, but also to permit the inclusion of new chapters to fill the more conspicuous gaps."

Volume I contains the following chapters: (1) Alicyclic Compounds and the Theory of Strain, by R. C. Fuson (51 pages). (2) Theory of the Structure and Reactions of Aromatic Compounds, by L. F. Fieser (98 pages). (3) Stereoisomerism, by R. L. Shriner, Roger Adams, and C. S. Marvel (256 pages). (4) Organometallic Compounds, by H. Gilman (83 pages). (5) Free Radicals, by W. E. Bachmann (53 pages). (6) Unsaturation and Conjugation, by C. F. H. Allen and A. H. Blatt (67 pages). (7) Open-chain Nitrogen Compounds, by C. D. Hurd (111 pages). (8) Molecular Rearrangements, by E. S. Wallis (82 pages). (9) Comparison of Chemical Reactivity, by H. Adkins (57 pages).

Again quoting from the preface, "For the sake of convenience in revising and expanding the book, the rapidly developing fields of natural products, relationship between physical properties and chemical constitution, valence and resonance have been grouped together in the second volume." Accordingly, Volume II contains the following chapters: (10) Natural Amino Acids, by H. T. Clarke (89 pages). (11) The Chemistry of the Pyrimidines, Purines, and Nucleic Acids, by Treat B. Johnson (70 pages). (12) Alkaloids, by Lyndon Small (96 pages). (13) The Anthocyanins and the Flavones, by Karl Paul Link (24 pages). (14) Carotenoids: The Polyene Pigments of Plants and Animals, by Marston Taylor Bogert (82 pages). (15) The Sterols, Bile Acids, and Related Compounds, by William H. Strain (179 pages). (16) Carbohydrates I, by M. L. Wolfrom (78 pages). (17) Carbohydrates II, by Albert L. Raymond (57 pages). (18) Carbohydrates III—Cellulose, by Emil Heuser (57 pages). (19) Modern Electronic Concepts of Valence, by John R. Johnson (61 pages). (20) Constitution and Physical Properties of Organic Compounds, by Wallace R. Brode and John A. Leermakers (117 pages). (21) Rotatory Dispersion, by P. A. Levene and Alexandre Rothen (67 pages). (22) The Signifi-

cance of Resonance to the Nature of the Chemical Bond and the Structure of Molecules, by Linus Pauling (71 pages).

A glance at the chapter headings suffices to reveal the scope of this work. A more careful study of the individual chapters will further reveal that the individual authors have devoted considerable time and effort to their tasks. Each chapter opens with an outline and closes with a number of references.

This two-volume treatise should be in the personal library of every graduate student in chemistry.

W. M. LAUER.

Die Theorie der Komplexität und der Allotropie. By A. SMITS. 22 x 16 cm.; xii + 372 pp.; 5 plates. Berlin: Verlag Chemie, 1938. Price: 19.50 RM.

Professor Smits in his book gives a full account of his theory of the complexity of the phases of a so-called simple substance (homogeneous allotropy), together with a detailed description of the experimental basis on which it is founded. The theoretical treatment is based on P, T, x diagrams and is illustrated by a number of clear and informative figures. The experimental work described includes a full discussion of the effects of intensive drying, and particular attention is devoted to sulfur trioxide, for which a large amount of experimental data is available. Other important systems are also discussed in sufficient detail to make the book a comprehensive monograph on its subject, which is one of considerable interest. The author has taken pains to make his account clear and understandable, and advanced students will be able to read the book with profit. Full references to literature are given, so that workers in cognate fields will be able to consult the original works. The book is very well produced and can be recommended to physical chemists.

J. R. PARTINGTON.

Der Smekal-Raman Effekt. Ergänzungsband, 1931-1937. By K. W. F. KOHL-RAUSCH. 15 x 22 cm.; ix and 288 pp. Berlin: Julius Springer, 1938. Price: 24 and 25.60 RM.

If testimony were needed for the industry of chemists and physicists, it is well supplied by this book.

The author states that some four thousand Raman spectra have been investigated, and approximately twelve hundred publications on the subject have appeared since the issue of his "parent" volume in 1931. Both the results themselves and the underlying development of theory are presented with completeness and with precision. In fact, readers of the original book will value the sense of balance which experience has brought about as knowledge has extended.

Perhaps the most valuable parts of these additional pages are those concerned with the optical model of the molecule, and with the "Polarizability theory" of Placzek. The advance in technique is well illustrated by the author's treatment of light sources and filters. In addition, there is a massive amount of tabular matter, admirably arranged.

Physical chemists will be grateful for this supplementary volume; with its help, the task of keeping up-to-date is considerably lightened.

F. I. G. RAWLINS.

Kontinuierliche Spektren. By W. FINKELNBURG. 24 x 18 cm.; xi and 368 pp. Berlin: Julius Springer, 1938. Price: 33 RM.

This scholarly work is undoubtedly a very valuable contribution to the study of continuous spectra. The author defines as continuous any spectrum not consisting of sharp lines. As a result of this a very wide ground requires to be covered.

This book is not only an admirable introduction to the whole broad field, it is also a complete report upon the present state of our knowledge of the subject. In the broader sense, the study of continua is rapidly acquiring more and more importance for physics, chemistry, engineering, and astronomy, and in order to meet the needs of such diverse possible readers, each chapter is preceded by a preliminary non-mathematical treatment. Summarizing chapters containing brief but complete surveys of the available experimental material are included.

The range covered is very wide and the treatment is thorough. A particularly clear and admirably concise section is that dealing with line widths, the many complex factors being clearly separated. Line broadening is treated as a limiting case of continua, a method of approach leading to important results. The contributions of the author himself in this field are well known.

The book contains much of interest to the chemist, since molecular continua naturally occupy the most important place. In that section which is effectively a report, detailed information is given about all the known diatomic and more complex molecular continua. Chapters upon the continuous spectra of liquids, solutions, and crystals are also included. Constant attention is given throughout to technical applications and to such varied aspects as photochemistry, flames, molecular dissociation, chemiluminescence, after-glows, etc.

The book closes with an extremely valuable list containing over seventeen hundred publications culled from practically every journal devoted to physics, chemistry, and astronomy.

Enough has been said to show that this treatise deserves a very warm welcome.

S. TOLANSKY.

Introduction to Physiological Chemistry. By MEYER BODANSKY. 4th edition. 14.5 x 23 cm.; 686 pp. New York; John Wiley and Sons, Inc., 1938. Price: \$4.00.

The fourth edition of this valuable textbook has been brought up-to-date by inclusion of much new material. The generally lucid style has been maintained, and the relation of the science to practical medicine has been kept in mind without in general sacrificing scientific accuracy or rigor. The most attractive feature of the book is perhaps the fact that the physiological aspects of chemistry are constantly brought to the fore.

In places the author has, in the opinion of the reviewer, made somewhat too dogmatic assertions on the basis of a review of portions of the literature. It is perhaps inevitable that this would occur in such an ambitious undertaking. An example of this defect occurs on p. 168 where the author outlines in full an application of the Donnan membrane equilibrium theory to the mechanism of the secretion of hydrochloric acid by the gastric glands. He says, categorically, "The soundness of this theory has been confirmed experimentally by Donnan, who has shown that, under such circumstances, hydrochloric acid may actually be "secreted" across a membrane." No modern physiological investigator of gastric secretion subscribes to the view that concentrations of hydrochloric acid such as found in gastric juice could possibly be formed by such a process. The earlier investigator cited was unfortunately unaware of many of the facts in the situation, particularly of the concentrations in plasma and gastric juice of certain constituents. Later in his discussion Bodansky cites some of the evidence which, if critically interpreted, disproves Donnan's contentions.

The biochemistry of the sterols and other phenanthrenes is inadequately treated. For example, the digitalis group of glucosides is discussed under carbohydrates, and although empirical formulas are given for many of them, no reference is made there to their phenanthrene structure. This is certainly the most important aspect

of their chemistry from a biological as well as chemical viewpoint. Since their aglucones have similar though less intense actions, it is obvious that the glucoside linkage is a minor point.

These critical details are not presented as serious defects, but to call attention to the fact that improvements are still possible. The mastery of any considerable portion of the subject matter in this book would represent a comprehensive grasp of modern physiological chemistry. The references to original and review literature are ample and well chosen. The index of 30 pages is very useful.

MAURICE B. VISSCHER.

Spectroscopy in Science and Industry. Proceedings of the Fifth Summer Conference on Spectroscopy and its Applications, Massachusetts Institute of Technology, Cambridge, Massachusetts. 134 pp.; 60 fig. New York: John Wiley and Sons, Inc., 1938.

Twenty-seven papers given at the 1937 conference have been collected in this volume in abbreviated form. They range in content from papers on physics, chemistry, metallurgy, biology, medicine, geology, and astronomy to papers on industry, in so far as these various fields use spectroscopy as a tool. Most of the leading American workers in applied spectroscopy are numbered among the authors. As Dr. George R. Harrison points out in the preface, the spectrograph is a tool whose use is rapidly increasing. Hence these conferences and also the present volume are very timely and should be of interest to many workers in scientific research, since they may learn that their own research may be furthered by application of spectrographic methods.

GEO. GLOCKLER.

The Elements of Quantum Mechanics. By SAUL DUSHMAN. 452 pp.; 82 fig. New York: John Wiley and Sons, Inc., 1938. Price: \$5.00.

This volume arose from a series of lectures given by the author during the summer of 1932 at the Ohio State University. The notes prepared for these lectures appeared in a series of articles in the *Journal of Chemical Education* (1935-36) and have now been collected and arranged in book form. Dr. Dushman's chief aim is to discuss the latest views of atomic and molecular structure as described in the new quantum mechanics, in such a simple fashion that the average reader, who knows only calculus, can profit by a study of this book. He spares no effort in trying to make the mathematical development clear and understandable. However, in order to grasp the full significance of these newer concepts, it seems that a knowledge of differential equations and methods of solving them is quite necessary. Evidently Dr. Dushman feels the same way about this situation, for in the second chapter he deals in detail with some simple differential equations as, for example, the case of the vibrating string. This procedure serves as an introduction to the famous Schroedinger equation of wave mechanics.

The content of the book is the usual one in such a beginning treatise: the Schroedinger equation, potential barriers, linear oscillator, rigid rotator, the hydrogen atom, van der Waals forces, the perturbation theory, the helium atom, the hydrogen molecule and its rotational and vibrational states, valency bonds, activation and resonance energy and radiation theory. But even so it is always an advantage to study these newer ideas from different authors. A rewording of a given topic by another writer may make its meaning clear to a reader who may have failed to grasp the logic of the development as rendered in the first book studied. Each chapter has an ample list of literature references. This treatise is therefore a welcome addition to the literature of this important subject.

The printing of the many mathematical formulae of most intricate design is excellent, and the figures are executed in admirable fashion. The clarity of expression on the part of the author and the admirable work done by the publishers make this volume welcome also to those workers who already have some knowledge of the newer logic. It has been a distinct privilege and a matter of enjoyment to review this book.

GEO. GLOCKLER.

German for Chemists. By J. H. YOE AND A. BURGER. 537 pp. New York: Prentice-Hall Inc., 1938. Price: \$4.50.

It has always been troublesome to find suitable reading material in teaching chemical German to students. This book supplies such material. It presupposes a good grounding in German grammar. The first part consists of practice in sentence structure, and both the German and the equivalent English sentences are given on opposite pages. Following this are sections of reading matter on inorganic chemistry (79 pages), organic chemistry (81 pages), analytical chemistry (61 pages), physical chemistry (62 pages), colloid chemistry (31 pages), chemical technology (64 pages), physiological chemistry (32 pages), and extracts from German books and magazines (32 pages).

The subject matter of each section, including the sentence structure matter, is progressive and is therefore an excellent review of the various fields of chemistry. The book is an excellent one and should find considerable use in teaching scientific German. Unless it is used not earlier than the third year in college it would not have the maximum value in teaching, because the student could not greatly benefit from sections dealing with material that is usually given in chemistry courses ordinarily taken during the last two years of college.

C. A. MANN.

Die Diffusionsanalyse am Blutplasmagel. By RUDOLF BUCHER. 123 pp.; 70 fig. 16 x 24 cm. Basel, Switzerland: Benno Schwabe and Co. Verlag, 1937. Price: 30 Swiss francs.

The author describes a method of transforming the blood plasma into a gel so that Liesegang rings can be obtained if a 5 per cent silver nitrate solution is allowed to diffuse into the potassium dichromate-impregnated gel. The method is applied to different physiological and pathological problems, so that the book is of interest both to colloid chemists and to physicians.

Colloid chemists find in this book one of the most important contributions to the problem of the Liesegang phenomenon made in recent years. The results are given in small type between pages 15 and 36. The author shows that the Liesegang phenomenon can be obtained in a quantitatively reproducible manner if certain experimental factors (e.g., temperature) are rigorously the same. Reproducibility means that the "Latenz Zone" (L. Z.) and the "Latenz Periode" (L. P.) have rather constant values if identical experiments are made with the same blood plasma. (L. Z. means the distance between the surface of the gel where the silver nitrate diffusion starts and the place where the first ring appears. L. P. is the time elapsing between the start of the diffusion and the appearance of the first ring.) This result removes much of the hazardous character inherent in the phenomenon up to now. Using a microtome the author carries out a topographical study of the gels formed. By this method he obtains very remarkable results with respect to the repartition of the crystalline precipitate of silver dichromate throughout the gel and to the size and number of the crystals inside and outside the Liesegang ring zones.

As far as the main purpose of the author is concerned, i.e., the attempt to use his method in physiology and pathology, a definite statement must be reserved until

more experimental material has been collected. The data already given show that the method is sensitive for very small changes in chemical composition and the colloid chemical behavior of the blood plasma. L. Z. and L. P. are different for different animals. They differ noticeably if the blood has been taken from different parts of a body. They change with the age of the organism and even with very slight changes in conditions of life. Their statistical mean values are different for the two sexes, etc. This extreme sensitivity of the method is at the same time its strength and its weakness.

It is regrettable that the author writes in a rather circumstantial style and uses without necessity a number of unusual German words and certain colloid chemical expressions of vague meaning.

The book is very well printed and illustrated, and contains numerous colored plates of remarkable technical quality.

WILFRED HELLER.

Chemical Kinetics. By FARRINGTON DANIELS. 6 x 9 in.; 273 pp.; 41 fig. Ithaca, New York: Cornell University Press, 1938. Price: \$3.25.

Although this book is based on lectures at Cornell University under the George Fisher Baker Non-resident Lectureship in Chemistry from February to June, 1935, it contains new developments in the field up to 1938. The object of the author has been to give the historical background as well as recent advances in chemical kinetics. In doing this he has followed the tradition of Baker Lectures by drawing illustrations from his own rich experiences in the laboratory.

The lectures have been addressed not only to experts but to students in all of the physical sciences. With this purpose in mind, experimental work has been stressed and mathematical discussion minimized. However, without employing it extensively Professor Daniels emphasizes repeatedly the use which is and can be made of mathematics in solving fundamental chemical problems.

The informal style of the book and the optimistic views of the author toward research are refreshing to the reader. Theoretical kineticists will profit from the review of many well-chosen experiments upon which modern theoretical developments are based. Research ideas abound throughout the book, and workers in other fields may see where chemical kinetics could help in solving their problems. To students and beginners in research this book will be especially inspiring. Unsolved research problems are so interspersed with seemingly equally difficult problems which have been worked out, that one is led to feel that the barriers to their ultimate solution are by no means insurmountable.

The first half of the book gives the elementary principles of kinetics as well as some details of experimental technique, while the second half is devoted to the use which may be made of such research tools as photochemistry, electrical activation, infrared spectroscopy, and isotopic tracers in this field.

F. E. BLACET.

W. A. NOYES, JR.

THIRD REPORT OF THE COMMITTEE ON PHOTO-CHEMISTRY,¹ NATIONAL RESEARCH COUNCIL

INTRODUCTION

HUGH S. TAYLOR

Department of Chemistry, Princeton University, Princeton, New Jersey

Received May 25, 1938

The First Report of the Committee on Photochemistry presented six papers dealing with the quantitative technique of photoreactions, the classical point of view with respect to these processes, and the relation between the physical concept of quantized absorption and the chemical processes which succeed such absorption. The Second Report summarized the researches of the physicist with respect to the absorption process and their implications in the primary absorption process in photochemistry, and gave some examples of the secondary processes consequent upon such initial processes of absorption. The discussion was necessarily confined to gaseous systems since, at that time, knowledge of the nature of the individual steps in condensed systems was less certain.

In the seven years that have elapsed since the previous report there have been a large number of contributions to the subject and the technique of photochemistry. These have served to broaden the bases upon which the science rests, to add to our techniques, to increase the quantitative nature of our knowledge, to permit an extension of our investigations to the more complex condensed systems, and to make possible a more scientific presentation of important problems in the field of applied photochemistry. Some phases of this activity are summarized in the present report, in which some eleven papers dealing with various topics are assembled. Professor Daniels reviews some of the contributions to experimental technique (page 701) and has prepared with the assistance of the Committee a critical table of quantum yields (page 713). Professor Rollefson has summarized the more recent aspects of the primary absorption process (page 733). In the analysis of reactions subsequent to the primary process, Professor Dickin-

¹ This Committee of the National Research Council, Division of Chemistry and Chemical Technology, is composed (1937-38) of the following members: Hugh S. Taylor, *Chairman*, Wilder D. Bancroft, Farrington Daniels, Roscoe G. Dickinson, Philip A. Leighton, Samuel C. Lind, George K. Rollefson. Contributions to this report have also been kindly prepared by Gertrud Kornfeld and Winston M. Manning.

son has discussed the correlation of photoprocesses in the gaseous phase with those in solutions (page 739). Recent researches into a variety of photoprocesses have considerably increased our knowledge of the secondary processes in which free radicals are produced in the primary process. From this standpoint Professor Leighton has summarized the researches on aldehyde and ketone photolysis (page 749), and the writer has dealt with the reactions in alkyl iodides, metal alkyls, mercury-photosensitized hydrogenations and decompositions of hydrocarbons, and the photolysis of azo compounds (page 763). Professor Rollefson has dealt generally with the problem of the evaluation of specific reaction rate constants (page 773), and the writer has summarized present knowledge in the case of ammonia decomposition (page 783) and the reactions involving the photochlorination of hydrogen and of carbon monoxide (page 789). Two final contributions in the domain of applied photochemistry, that of Dr. Gertrud Kornfeld on "The Action of Optical Sensitizers on the Photographic Plate" (page 795) and of Dr. W. M. Manning on "Photosynthesis" (page 815), complete the series of contributions.

It is not intended that this report shall represent an exhaustive summary of the photochemical work which has accumulated since the issue of the preceding report. Many publications in the field have not been covered, even though the papers here reviewed exceed six hundred. Other topics undoubtedly merit attention equal to that given to the subjects here discussed. That this is so indicates both a healthy state of photochemical science and a continuing task for the Committee.

EXPERIMENTAL TECHNIQUE IN PHOTOCHEMISTRY¹

FARRINGTON DANIELS

Department of Chemistry, University of Wisconsin, Madison, Wisconsin

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Ten years ago, when G. S. Forbes (12) wrote the first report of the Committee on Photochemistry of the National Research Council, most of the principles of experimental photochemistry had been enunciated, but quantitative photochemical measurements had just begun. Since that time a few new techniques have been invented and old ones have been improved; over a hundred quantitative researches have given us the amount of chemical action produced and the amount of radiation of restricted wave length used. It is gratifying that workers in different laboratories are now able to check each other's results when the working conditions are the same.

The production of monochromatic light, the measurement of the energy absorbed and the chemical reaction produced, and the determination of the nature of the spectrum are the chief problems of the experimental photochemist. Because the monochromatic light is of reduced intensity, the first problem has led to the development of semi-micro methods of analysis.

It is not the purpose of this report to give a complete description of the methods used in photochemical investigations, for they may be found in the first report of this Committee (12) and elsewhere (10, 11, 15), or to include a bibliography of researches that have been published on this subject. It is planned merely to build on the first report giving trends of the past decade in experimental photochemistry, to record advances in technique, and to refer to a few selected researches where further details and additional references may be found.

LIGHT SOURCES

Arcs

The quartz mercury-vapor arc lamp is the almost universal standard for photochemical investigations when monochromatic light is necessary. It can be used, however, for only a few selected wave lengths extending from 2000 Å to 10,000 Å. Several types of arc lamps are commercially available.

¹ Contribution No. 1 to the Third Report of the Committee on Photochemistry, National Research Council.

A small 80-watt lamp which operates on alternating current with a transformer has been put on the market recently at a low price. It is about 4 mm. by 20 mm. and is suitable for many photochemical experiments.

Intense light, for illuminating monochromator slits or small cells, is best supplied by capillary lamps (9, 21), in which the light is concentrated in a small region. These lamps are so inexpensive that one can afford to run them at a heavy overload, even though their life is short. At these overloads, up to a kilowatt in 10 cubic millimeters of space, the lamps must be water-cooled.

For the line at 2537 Å. a high-voltage lamp filled with mercury vapor and argon and neon is particularly suitable (32, 45). It operates on alternating current at about 6000 volts. Eighty-eight per cent of all the radiation is given off at this wave length, all the other lines being quite weak.

Arc lamps of other metals comparable in intensity and practicality with the mercury lamp have long been needed. Sodium arc lamps in glass are now available ("Sodium Lab-arc") and are useful for many purposes, but the demands for high intensities in photochemical work are hardly met by them.

Neon lamps are also available in convenient form for producing red light, but it is difficult to obtain a highly concentrated radiation from a small area of these lamps.

Quartz capillary lamps of cadmium, zinc, thallium, bismuth, and lead can be made to give light at several different lines which is practically as intense as that of the capillary mercury lamp. These lamps (25) are troublesome to make and operate, however, and the intensity falls off because of the formation of an inner coating of silicate; moreover they break when the current is turned off.

Tungsten filament lamps are used when continuous light is needed in the red or throughout the visible spectrum. Concentrated filaments are preferred. The intensity of the lamps may be increased considerably by operating them for short times at voltages considerably above their rated voltage.

Steadiness of a lamp can be achieved through the use of storage batteries, storage batteries floated across a dynamo, an isolated dynamo, or a dynamo operated by a synchronous motor. Voltage regulators are available operating with electron tubes or with a ballast coil of iron wire in series with the lamp.

Sparks

For the shorter ultraviolet in the region of 2000 Å. and below, spark discharges between electrodes of aluminum, magnesium, and zinc are used (13, 26). Several types have been described. It is possible, though troublesome, to obtain from them intensities equal to those of the mercury

lamp. Large transformers up to 10,000 volts and 5 kilowatts have been used together with large condensers. A blast of cooling air is directed against the spark. The noise and oxide dust are seriously annoying. Large discs of metal rotating at right angles may be used to confine the arc to one position and yet give constantly replaced surfaces (50).

PRODUCTION OF MONOCHROMATIC LIGHT

Filters

Filters are the cheapest and most convenient means for restricting the radiation to a narrow range of frequencies. A complete assortment of glass filters is available with which the various lines of mercury, helium, or hydrogen can be isolated (19).

A filter of chlorine and bromine gas in quartz is used for filtering out the longer ultraviolet and leaving the 2536 Å. line of mercury. Acetic acid cuts off all radiation below 2300 Å. Additional filters for specific purposes can be made from solids, liquids, and solutions, the absorption characteristics of which can be found in the literature (11, 18, 27).

An excellent set of laboratory filters for the mercury lamp has been assembled by Bowen (5).

The infrared radiation is practically completely absorbed by 4 cm. or more of a 1 per cent aqueous solution of copper sulfate (6).

The Christiansen filter (11) consists of a mass of particles of glass or quartz in a bath of liquid having the same refractive index at a given wave length, but a different dispersion. Particles of crown glass (1 to 2 mm. in size) are immersed in a mixture of carbon disulfide and benzene of such a composition that it will have the same refractive index at 5000 Å., for example. A beam of light of this wave length will pass through, but light of all other wave lengths will be dispersed. A different composition will pass light of a different wave length. Close temperature control is essential and the range of wave lengths transmitted is not as narrow as might be desired, but the filter can be adjusted to any wave length and the loss of energy in the transmitted light is not great.

Monochromators

Monochromators, their requirements, and their limitations, have been described by Forbes (12). Large aperture and short focus are desirable for photochemical work (16, 22) in order to conserve as much energy as possible. Glass and quartz prisms are commonly used, but large hollow prisms filled with a liquid are satisfactory. Ethyl cinnamate is an excellent liquid for this purpose on account of its high refractive index and its ability to withstand photochemical decomposition. Water is used sometimes, but its refractive index is comparatively low. These liquid prisms

give lines which are slightly distorted unless the prisms are thermostated with great care, but they are satisfactory for most photochemical work and they are comparatively inexpensive. A large monochromator using a water prism has been described by Harrison (20).

A double monochromator, in which the light from the exit slit of the first one passes into the entrance slit of the second, is much more effective than a single one in giving monochromatic light of great purity. Obviously the intensity is decreased. A double monochromator making use of ethyl cinnamate prisms is on the market.

In the focal isolation method the light of different wave lengths is separated by refraction with a lens instead of a prism. The light of short wave length is brought to a focus closer to the lens and passes through a small hole in a plate, while the longer rays are stopped. The apparatus is simpler to construct and in the short ultraviolet it is probably more effective. It has been used in several investigations making use of spark emission in the ultraviolet (23, 50). This method has been compared critically with the monochromator method (23).

When mirrors are used, as with the Wadsworth mounting for a monochromator, the sputtering of a clean glass surface with aluminum or other vapor in a vacuum is found to be superior to the ordinary silvering process.

MEASUREMENT OF RADIATION

Thermopiles are usually the simplest and best instruments for measuring the intensity of radiation. Bismuth-silver, copper-constantan, and tellurium-platinum are among the combinations of metals which have been used, each being soldered to a thin, blackened metal receiver.

High sensitivity is not a very important characteristic of a thermopile, because the limiting factor in photochemical measurement is more likely to be the accuracy of the chemical analysis. The thermopile should be absolutely reproducible, with little drifting of the zero point. The theory and practice of thermopile construction have been discussed critically by Leighton and Leighton (32). The construction of a small thermopile has been described by Beckmann and Dickinson (1). The ordinary linear thermopile is smaller than the chemical reaction cell behind which it is placed, and it is necessary to move the thermopile over the whole area in order to obtain an average value. Large-area thermopiles which do their own integrating are simpler for photochemical investigations. The thermocouples, thoroughly protected with glyptal lacquer, are attached with de Khotinsky cement to the back of a blackened receiver 10 by 40 mm. in area.

High sensitivity galvanometers of the d'Arsonval type, giving deflections at 1 meter of 5 to 10 mm. per microvolt, are sufficiently sensitive. Galvanometers of the Paaschen type are more sensitive but more trouble-

some. If necessary the sensitivity can be pushed to the theoretical limit of 10^{-10} volt imposed by the Brownian motion of the electrons (28), by amplification with two galvanometers. A beam of light from the first galvanometer hits a thermopile or photoelectric cell connected to a second galvanometer, and the system is so arranged that the deflection of the second galvanometer is directly proportional to that of the first (36).

Calibration

The energy of radiation is now determined in nearly all photochemical investigations by means of the standard carbon-filament lamps obtainable from the U. S. Bureau of Standards (7, 10). Calibration of a thermopile and galvanometer is quickly and easily accomplished, and absolute values are reliable to within about 2 per cent.

As secondary standard, the uranyl oxalate actinometer (30) is widely used. It is desirable to cross check all photochemical measurements with this simple actinometer. A solution 0.05 molar in oxalic acid and 0.01 molar in uranyl sulfate is titrated with potassium permanganate. The following quantum yields (molecules reacting per quantum) apply at 25°C.:

Wave length (Å)	2550	2650	3000	3130	3660	4060	4350
Quantum yield	0.60	0.58	0.57	0.56	0.49	0.56	0.58

When the light is feeble the length of exposure may become impractically long, but more sensitive actinometers such as the mercuric oxalate actinometer, which depend on chain reactions, are not sufficiently reproducible or reliable for quantitative measurements.

Photoelectric cells

Photoelectric cells and electron tube amplifiers are easy to use and are much more sensitive than thermopiles, but they are selective and one must be sure that they give responses which are directly proportional to the intensity at the particular wave length used. They should be calibrated against a thermopile at each wave length.

In the study of ultraviolet radiation of extremely low intensity, Geiger counters are used in which a photoelectric surface emits electrons into a gas space between charged electrodes. A system of electron tubes amplifies greatly the ionization current produced each time that a photoelectron is shot out.

REACTION CELLS

A satisfactory photochemical cell should have clear windows with no distortion of light, and the light should fill practically the whole cell. Practices vary, but when a good thermopile is placed immediately behind the cell it is usually preferable to have the depth of the cell and the concen-

tration such that a measurable part of the light is transmitted past the cell. When all the light is absorbed within the cell the calculations are somewhat simplified, but then the intensity at the front and back of the cell varies from full intensity to zero, a fact which may cause uncertainties if the intensity of the light affects the quantum yield. When a dark reaction is involved the correction factor may become too large if there is such a large excess of material as to absorb all the light.

Glass or quartz cells are conveniently made by fusing polished discs into tubing of just the right size. Both windows should be at right angles to the path of the light. Flasks or tubes can be used for approximate work when the light energy is measured with an actinometer in the cell.

The cell should be so designed that nearly all of the contents of the cell are in the path of the light. Rectangular or trapezoidal cells are preferred, and they can be made to order either in quartz or in Pyrex.

Stirring is usually unnecessary in gaseous reactions, but it may be necessary for liquid reactions, particularly if a dark reaction is involved or if the reaction is influenced by intensity of light or concentration of material. Stirring should be omitted only in case experiments show that it is not necessary under the conditions of the experiment.

CHEMICAL ANALYSIS

The requirements for monochromatic light reduce the energy intensity to such an extent that micro or semi-micro methods of analysis are often necessary. One of the most successful micromethods for gas analysis has been developed by Blacet and Leighton (2, 3, 4), using a small bead of solid absorbent,—phosphorus for oxygen, phosphorus pentoxide for water, silver oxide for carbon monoxide, and copper oxide and potassium hydroxide for hydrogen, and other absorbents. Only 0.25 to 1 cc. of gas is needed for a complete determination.

More micromethods are needed, particularly for complex organic compounds.

The removal of gas for analysis offers a problem, particularly when the gas is at reduced pressure. Toepler pumps, which utilize the filling and emptying of a mercury reservoir, are often used (43). Sometimes the gas is pumped out and frozen in a small tube surrounded with liquid air. Boiling points and freezing points are always useful in identification. Titration methods of precision such as iodimetry find frequent use. Electro-titrations have been developed to a point which makes possible increased accuracy in the study of some photochemical reactions. Conductance methods are applicable sometimes (47).

In gaseous reactions pressure change has been the most common method for following the course of a reaction. Obviously the method is applicable

only when there is a change in the number of molecules and when the stoichiometrical reaction is known to be fairly simple. The pressure is usually followed in a constant-volume cell through a flexible diaphragm of glass or quartz. Many different types are available (8, 42).

The application of Beer's law to the determination of the chemical change is receiving increasing application. The absorption of light constitutes one of the simplest methods of analysis and is particularly desirable because it does not disturb the reacting system nor demand the removal of samples. Frequently the same thermopile measurements may be used for the determination of both energy absorption and chemical change. If Beer's law applies, the concentration at any time can be calculated directly from the absorption coefficient, or interpolation may be made on a logarithmic graph. Even when Beer's law does not apply, graphical interpolation on an experimentally determined logarithmic graph will give the concentration.

Thermopile-galvanometer readings may be summed up over long periods of time to give both energy absorbed and chemical change produced (24).

The analysis by absorption of light may be applied not only in the case of the light used in the photochemical reaction but to any other wave length. For example, the production of iodine or chlorine in a photolysis by ultraviolet light can be followed by the absorption of light in the visible. It must be proved experimentally that the materials actually absorbing the light are directly involved in the reaction. For example, Vesper and Rollefson (48) showed that earlier calculations involving the chlorination of monobromotrichloromethane were erroneous because it had been assumed that chlorine was the only substance absorbing the light, whereas in reality it was being absorbed by a bromine-chlorine compound having an entirely different absorption spectrum. Analysis by infrared absorption has been very accurate and successful in the case of the nitrogen oxides (49) and carbon dioxide (34).

Direct analysis with a colorimeter is often possible, and the increasing use of the photoelectric colorimeter will certainly find further application in photochemical investigations.

HIGH AND LOW TEMPERATURES

Most photochemical investigations have been limited to temperatures in the neighborhood of room temperature. Data over a wide range of temperature are needed. Particularly with the new interest in free-radical chain reactions it is desirable to obtain quantum yields and chain lengths at high temperatures,—at 300° to 400°C., for example (29, 35). Special techniques have been developed. It is a good plan to have the thermopile back of the heated reaction chamber completely immersed in water to prevent radiations from the heated walls striking the thermopile.

Low temperature halogenations have been carried out in "freon" surrounded by dry ice (14).

ABSORPTION SPECTRA

Intelligent planning of a photochemical investigation demands first a full knowledge of the regions in which light is absorbed. Spectrograms are essential for this purpose.

Much can be learned from absorption spectra concerning the primary photoprocess. The existence or non-existence of fine structure in the spectrum is often sufficient to decide between different photochemical mechanisms. Grating spectrographs give the greatest dispersion, but prism spectrographs of the best type are often adequate. The fine structure of the spectrum of acetone vapor offers an illustration (38, 39).

The more complex organic compounds and substances in the liquid phase are not likely to show fine structure, but a complete knowledge of the various absorption bands is helpful. Sometimes the finer details of the spectrum can be brought out by lowering the temperature of the absorbing substances with dry ice or liquid air.

Absorption spectra can be mapped in the usual way by splitting the beam of light into two paths, passing one through the absorbing material and reducing the intensity of the other until the two become equal. On a photographic plate the two are matched. Again the amount of absorption can be determined by the density of the lines or regions on the photographic plate as measured with a photoelectric cell or thermopile. Excellent recording apparatus is available for giving in full detail the intensity of absorption throughout the spectrum.

An important new development is the adaptation of the photoelectric cell to the direct determination of the percentage absorption in the different parts of the spectrum (53). Quantitative absorption measurements on chlorophyll have been obtained by this means (52) without the uncertainty of the photographic plate. In some ways this method is less expensive and more direct than the photographic method.

The emission spectra of fluorescent materials may give information regarding the photomechanisms. Since the light is weak, large apertures and long exposures are necessary with a photographic plate. Quantitative measurements of the energy emitted in fluorescence may be made with the photoelectric cell (53).

For the light needed in making absorption spectra tungsten filaments are suitable down to about 3600 Å., but the intensity is low at the shorter wave lengths. Quartz windows may be attached to the glass bulbs surrounding the filament. The iron arc gives many lines throughout the whole spectrum and is widely used in absorption spectra, but it is obviously unsuited for studying fine structure.

Improvements have been made in continuous sources of light in the ultra-violet. The spectrum of molecular hydrogen is most commonly used. Vessels are so arranged that an intense electrical discharge is passed through hydrogen at a low pressure in a tube which allows recombination of the atoms by collision with a metallic surface. An efficient tube of simple design has been described by Munch (37).

Isotopic tracers

The new techniques by which atoms can be traced through chemical reactions by means of radioactivity or abnormal (isotopic) atomic weights are destined to settle many problems of photochemistry. To date only a few experiments of this type are on record.

Taylor and Jungers (46) mixed deuterium with ammonia and mercury vapor and subjected the mixture to illumination with the resonance radiation at 2536 Å. Deuterium entered the ammonia under the influence of the radiation, and the results showed that the low quantum yield obtained in the photolysis of ammonia is due to the recombination of hydrogen atoms and the NH_2 radicals formed by the photochemical reaction.

Leighton and Mortensen (33) used radioactive lead in their study of the mechanism of the photolysis of lead tetramethyl.

Free radicals

Many photochemical reactions are now believed to involve the production of free radicals as a first step. There is a great deal of indirect evidence and some direct evidence for this theory. A test has been applied, for example, in the photolysis of acetone, in which removal of a lead or antimony mirror is used to support the view that free methyl radicals are produced in the photolysis (40, 44).

The existence of OH and other free radicals in the electrical discharge has been proved by characteristic absorption bands (17).

One of the most complete researches on absorption has given experimental proof of the production of iodine atoms when iodine molecules are illuminated. Rabinowitch (41) has described a delicately balanced colorimeter, with an amplifying circuit of electron tubes, which measures with great accuracy the change in absorption produced by a photochemical reaction.

The conversion of ortho-para hydrogen has been used also as a test for the independent existence of free radicals containing an odd number of electrons (51).

REMARKS

Quantitative methods for measuring photochemical reactions are now well established, but more intense sources of monochromatic light are

needed. Also, the further development of the spectroscopy of polyatomic molecules will lead to advances in photochemistry. Improvements are needed in methods for the analysis of the complex products of photochemical reactions. Special care must be exercised in certain reactions to remove impurities such as oxygen and moisture, which sometimes affect the reaction. Interesting developments are to be expected in photochemical studies at high and low temperatures, and at low gas pressures.

Greater accuracy in determining quantum yields is useless unless the conditions of temperature, pressure or concentration, and light intensity are clearly defined.

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A TABLE OF QUANTUM YIELDS IN EXPERIMENTAL PHOTOCHEMISTRY¹

FARRINGTON DANIELS

Department of Chemistry, University of Wisconsin, Madison, Wisconsin

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In the early development of quantitative photochemistry it was believed by some that the Einstein relation would apply in many cases not only to the primary process of photoexcitations but to the overall reaction as well. Quantum yields were summarized with the purpose of testing this hypothesis. Any hope of simplicity in chemical kinetics disappeared long ago, and the present table has been assembled not to emphasize the almost universal occurrence of secondary effects which follow the primary process of quantum absorption, but to record the experimental facts of photochemistry in the simplest possible manner. The primary excitation is usually followed by rearrangements and degradation of the energy as heat, by reverse or competing reactions which make the overall quantum yield less than unity, or by continuing reactions which produce a chain and give a value greater than unity. Sometimes it is possible to study these factors from the magnitude of the quantum yield and its response to influences such as temperature, wave length, concentration, and chemical reagents.

The amount of chemical reaction produced by the absorption of radiation will change with the duration of exposure, the intensity of the light, the thickness and condition of the absorbing material, and other factors. The fundamental simple relation between light and chemical action, however, is the quantum yield Φ , i.e., the number of molecules of substance reacting for each quantum of radiation, or photon, absorbed. When this is known the extent of the chemical reaction produced by the absorption of a given amount of light is easily calculated.

In table 1 are summarized the findings of most of the quantitative photochemical researches in which the results are expressed in terms of quantum yields. Many excellent researches are not included, simply because the results were not given in these terms. Photochemistry has been greatly stimulated by hypotheses in chemical kinetics, and the testing of these hypotheses has been the chief aim in many cases. For

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TABLE 1
Table of quantum yields in photochemistry

REACTION AND PRODUCTS	SOLVENT	ABSORBER	WAVE LENGTH \AA	TEMPERATURE $^{\circ}\text{C}$.	QUANTUM YIELD	REMARKS AND REFERENCES*
Acetaldehyde decomposition $\rightarrow \text{CH}_4; \text{CO}$	Gas	CH_3CHO	2537	30	0.9	Polymerization accompanies reaction; Φ changes with pressure; some hydrogen produced (12, 71) (69)
			2804	30	0.5	
			3130	30	0.2	
			3130	310	300	
Acetaldehyde decomposition $\rightarrow \text{CH}_4; \text{C}_2\text{H}_6; \text{CO}$		CH_3CHO		300	103 ⁽¹⁾	⁽¹⁾ at 100 mm.; ⁽²⁾ at 700 mm.; Φ decreased by addition of NO
					409 ⁽²⁾	
				350	196 ⁽¹⁾	
					710 ⁽²⁾	
				400	338 ⁽¹⁾	
				450	1374 ⁽²⁾	
Acetic acid decomposition $\rightarrow \text{CH}_4; \text{CO}_2$	H_2O	CH_3COOH			589 ⁽¹⁾	† (84)
					2278 ⁽²⁾	
			1850-2300		0.5	
Acetone decomposition \rightarrow $\text{C}_2\text{H}_6; \text{CO}$	Gas	$(\text{CH}_3)_2\text{CO}$		56	0.17	680-760 mm. (27) 10 per cent CH_4 (89) (135) 1 At 0.2 mm. At 52.3 mm. (58)
			3130-2650	60	0.2	
			3130	60	0.4	
			2480-2770	60	0.2-1	
			2200-3300	60-100	1	
			1900	160-400		
				25	0.66	
					0.46	

Acetone decomposition → alcohol, etc.	$n\text{-C}_4\text{H}_{10}$	$(\text{CH}_3)_2\text{CO}$	2480-3135	0.27	10 per cent solution (21)
Acetone hydrolysis → CH_3COOH ; CH_4	H_2O	$(\text{CH}_3)_2\text{CO}$	Hg arc	(0.12) (0.17)	In 0.05 molar solution; decreases in more concentrated solu- tions (97)
Acetylene polymerization → $(\text{C}_2\text{H}_2)_n$	Gas	C_2H_2	2150	9.2	(77)
→ $(\text{C}_2\text{H}_2)_n$		Hg	2636	6.5	Mercury-sensitized; pressure 1-40 mm. (61)
→ $(\text{C}_2\text{D}_2)_n$		Hg		5	
Acraldehyde decomposition → CO ; C_2H_2	Gas	$\text{C}_3\text{H}_4\text{O}$	3130 3660	0.15 0.01	(115)
Acraldehyde polymerization → $(\text{C}_3\text{H}_4\text{O})_n$		$\text{C}_3\text{H}_4\text{O}$	2537-3660 2537 2654 2804 3020 3130 3660 3130 3660	<0.04 19 19 10 1 0.5 0.3 2.3 0.4	Banded absorption 3130-3660; continuous absorption below 2804 (10) (115)
Allene polymerization → $(\text{H}_2\text{C}:\text{C}:\text{CH}_2)_n$	Gas	$\text{H}_2\text{C}:\text{C}:\text{CH}_2$	Hg arc	2.5	(78)
Amino acids deamination → NH_3 ; $\text{RC}(\text{OH})\text{COOH}$	H_2O	Alanine Betaine Glycine	Hg arc	1.0 0.5 0.9	(129)

* A reference, given in parentheses in the last column, applies to all the material between it and the preceding reference.

TABLE 1—Continued

REACTION AND PRODUCTS	SOLVENT	ABSORBER	WAVE LENGTH Å	TEMPERA- TURE °C.	QUANTUM YIELD	REMARKS AND REFERENCES
Ammonia decomposition \rightarrow N_2 ; H_2	Gas	NH_3	2099-2194	20	0.14	Pressure 1-8 atm.
				400	0.6	(95)
			2000-2200	19-400	0.25	Followed by ortho-para hydro- gen conversion (39)
			2026-2138	21-31	0.10	At 0.1 mm.
	Liquid Gas	NH_3 Hg			0.30	At 65 to 120 mm.
					0.18	At 760 mm. (133)
			1990		<0.02	(94)
			2537		0.87	Mercury-sensitized; Φ ap- proaches zero at low pressures (126)
Anthracene polymerization $\rightarrow (C_{14}H_{10})_2$	C_6H_6	$C_{14}H_{10}$	3130-3665	80	1 to 0 (0.5)	Reaction reverses in dark (128)
Arsine decomposition $\rightarrow As$; H_2	Gas	Hg	2537	24-27	1.03	Mercury-sensitized (107)
Azomethane decomposition $\rightarrow C_2H_6$; N_2	Gas	$(CH_3)_2N_2$	3665	20-226	1.0	At 181 mm.
					0.77	At 684 mm.
			2540		0.25	Primary products CH_3 and N_2 ;
			2080		0.24	products complex (43, 28)
Bromination of acetylene $\rightarrow C_2H_2Br_2$	Gas	Br_2	4358-5791	20	3000	
				150	500	(19)

Bromination of acetylene dichloride \rightarrow $\text{CHClBr} \cdot \text{CHClBr}$	Gas CCl_4	Br_2 Br_2	4060-5460 4060-5460	30-40 30-40	(100) (1.8-3.0)	(47)
Bromination of benzene \rightarrow $\text{C}_6\text{H}_5\text{Br}$	Liquid	Br_2	3000-5500	17-50	0.4-0.9	(98)
Bromination of cinnamic acid \rightarrow $\text{C}_6\text{H}_5\text{CHBr} \cdot \text{CHBrCOOH}$	CCl_4	Br_2	4060-5460	0-30	1-30	Saturated with air; increases with concentration of bromine; in absence of oxygen Φ is large (5)
Bromination of hydrogen \rightarrow HBr	Gas	Br_2	5000-5780	<150 >150	0 1-2	Several factors involved (16, 60)
Bromination of tetrachloroethylene \rightarrow $\text{C}_2\text{Cl}_4\text{Br}_2$	Liquid	Br_2	4360	25-135	0.1 to 24	Depends on concentration of products and on oxygen (134)
Bromophosgene decomposition \rightarrow CO ; Br_2	Gas	COBr_2	<3200	10-40	1	(103)
Chlorination of benzene \rightarrow $\text{C}_6\text{H}_5\text{Cl}$	Gas	Cl_2	3660 and 3130	25	12-46	Depends on pressures; Cl_2 , 95-126 mm.; C_6H_6 , 8-40 mm. (110)
Chlorination of formic acid \rightarrow HCl ; CO_2	Gas	Cl_2	3660	20-30	2000	HCOOH , 65-100 mm.; Cl_2 , 200-300 mm. (131)
Chlorination of chlorom for \rightarrow CCl_4 ; HCl	Gas	Cl_2	4358	60	300	Cl_2 , 77 mm.; CHCl_3 , 32-128 mm. (105)

TABLE 1—Continued

REACTION AND PRODUCTS	SOLVENT	ABSORBER	WAVE LENGTH λ	TEMPERATURE °C.	QUANTUM YIELD	REMARKS AND REFERENCES
Chlorination of cinnamic acid $\rightarrow C_6H_5CHCl \cdot CHClCOOH$	CCl_4	Cl_2	3660	25	2.4	Depends on Cl_2 concentration. Probably oxygen-inhibited (9)
Chlorination of dichlorobenzenes $\rightarrow C_6Cl_5H; HCl$	Gas	Cl_2	3660	20	0.39	Depends on dichlorobenzene pressure (40)
Chlorination of dichloroethylene $\rightarrow CHCl_2 \cdot CHCl_2$	Gas	Cl_2	4360	85-95	7000	Cl_2 , 100 mm. (86)
Chlorination of hydrogen $\rightarrow HCl$	Gas	Cl_2	3660 3030-4360 4300-5000	17-27 30	$(<10^6)$ 4×10^6	Depends on many factors; inhibited by O_2 and HCl (99) (25) Silver walls. Oxygen removed (17)
Chlorination of methane $\rightarrow CH_3Cl_{4-x}$	Gas	Cl_2	2537 4360		(100,000) (24)	
Chlorination of pentane $\rightarrow C_5H_{11}Cl; HCl$	Gas	Cl_2	3660	25	(190)	Oxygen excluded (114)
Chlorination of sulfur dioxide $\rightarrow SO_2Cl_2$	Gas	Cl_2	4200		(1)	(18)
Chlorination of tetrachloroethylene $\rightarrow C_2Cl_4$	Gas CCl_4	Cl_2 Cl_2	4360	40	300-500 300-500	In absence of oxygen (31)

Chlorination of toluene \rightarrow $C_6H_5CH_2Cl$	Liquid	Cl_2	4050	-80	(27)	(20)	
Chlorination of trichlorobromomethane $\rightarrow CCl_4$; Br_2	Gas	Cl_2	3660	28	30	(119)	
Chlorine monoxide decomposition $\rightarrow Cl_2$; O_2	Gas	Cl_2O Cl_2O or Cl_2	2350-2750 4030-4360 4360	20 10-40	4.5 2 >1.8	(104) (14) ClO_2 formed also (32)	
Chlorine dioxide decomposition $\rightarrow Cl_2$; O_2 $\rightarrow Cl_2$; O_2	Gas	ClO_2 Br_2	3660 4360 5460	18 31 15	3.1 2.7 3	Addition of water vapor gives reproducible results (112) Bromine-sensitized (112)	
Cinnamic acid isomerization	H_2O	$C_6H_5CH=CHCOOH$	3130	28	0.6	0.003 M solution (117)	
l-cinnamic acid isomerization	H_2O	$C_6H_5CH=CHCOOH$	3130	28	0.2	0.003 M solution (117)	
Citraconic acid isomerization	H_2O	$CH_3C(COOH)=CHCOOH$	3130	18	0.2	0.01 M solution (117)	
Crotonaldehyde decomposition $\rightarrow RH$; R_2 ; H_2 ; CO	Gas	Crotonaldehyde	2400 and 3660	30	<0.02	(11)	

TABLE 1—Continued

REACTION AND PRODUCTS	SOLVENT	ABSORBER	WAVE LENGTH Å	TEMPERATURE °C.	QUANTUM YIELD	REMARKS AND REFERENCES
Cobalt potassium oxalate → CO ₂ ; CO; H ₂ O	H ₂ O	K ₂ Co(C ₂ O ₄) ₂	3660 4050 4360	10-22	(1.5) (0.9) (0.6)	(121)
Diazomethane decomposition → CH ₄ ; N ₂	Gas	CH ₃ N ₂	3650 and 4360	25	4	(62)
Dibromotetrachloroethane decomposition → C ₂ Cl ₄ ; Br ₂	Gas	Br ₂	4360	100 125 150	0.5 3.2 15.2	Bromine-sensitized 5-43 mm. Products decrease Φ (22)
Dimethyl ether decomposition with acetone → CH ₄ CO; H ₂	Gas	(CH ₃) ₂ CO	3130	200-400	5-230	Depending on pressure and light intensity (70)
Ethyl iodide decompositions → C ₂ H ₁₀ ; I ₂	Liquid	C ₂ H ₅ I	2537 2654 3130 2610 2026 2026 2610 2026 2026 2610	5-58 25	0.41 0.38 0.31 0.01 0.1 0.03 0.6 0.1 0.24 0.6	Independent of temperature (92) At 90 mm. At 0.1 mm. (130) At 95 mm. (132) (130)
Ethylene iodide decomposition → C ₂ H ₄ ; I ₂	C ₆ H ₆					
	CCl ₄	C ₂ H ₅ I ₂	3030 and 3130	25	0.76	0.036 M solution. With cor- rection for retarding effect of iodine produced $\Phi = 1$ (29)

Formaldehyde decomposition → H ₂ ; CO	Gas	HCHO	2540-2640 3030-3130 3340-3650 Hg arc	0.9 1.1 0.7 100	(91) (1)
Formic acid decomposition → CO ₂ ; H ₂ → CO ₂ ; CO; H ₂ ; H ₂ O		(HCOOH) ₂ HCOOH	1900-2540 23-134	1 1	Independent of temperature and pressure (CO + H ₂ O)/(CO ₂ + H ₂) varies with wave length (51)
Fumaric-maleic acid transformation	H ₂ O	$\begin{array}{c} \text{HCCOOH} \\ \parallel \\ \text{HOOCCH} \end{array}$	2070-2820 3130	(0.1) 0.1	0.01 M (123) 0.01 M (117)
Hydrazine decomposition → NH ₃ ; N ₂ ; H ₂	Gas	N ₂ H ₄ Hg	1990 2547	1.0 1.7 (13)	At 2 mm. At 14 mm. (127) Hg-sensitized (36)
Hydrogen azide decomposition → NH ₃ ; N ₂ ; H ₂	Gas	N ₃ H	1990	1.74-3.89	Pressure 0.3-131 mm. (7)
Hydrogen azide decomposition → NH ₃ ; N ₂ ; H ₂	Gas	Hg	2537	2.86	Hg-sensitized (83)
Hydrogen bromide decomposition → H ₂ ; Br ₂	Gas	HBr	2070 2530	2 2	(122)
Hydrogen iodide decomposition → H ₂ ; I ₂	Gas	HI	2070-2820	2.0 1.84 2.0	Simple photochemical reaction (76) (15) (125)
	Liquid C ₆ H ₁₄		27		

TABLE 1—Continued

REACTION AND PRODUCTS	SOLVENT	ABSORBER	WAVE LENGTH λ	TEMPERATURE °C.	QUANTUM YIELD	REMARKS AND REFERENCES
Hydrogen peroxide decomposition \rightarrow H_2O ; O_2	H_2O	H_2O_2	2750–3660 3130	2–26 28	20–500 (1)	Depending on concentration and pH (3) At infinite dilution (55)
Hydrogen sulfide decomposition \rightarrow H_2 ; S	Gas	H_2S	2050		2	At 250 mm. (113)
Hypochlorous acid decomposition \rightarrow HCl ; $HClO_2$; O_2	H_2O	$HClO$	3660 4360		(2) (2)	0.03–0.05 M solution (2)
Iodine with $N_2CHCOOC_2H_5$ \rightarrow N_2 ; $I_2CHCOOC_2H_5$	CCl_4	I_2	5460 and 5780	18	<2	Proportional to I_2 in dilute solutions (87)
Iodine with ferricyanide ion \rightarrow $Fe(CN)_6^{--}$; I^-	H_2O	I_3^-	5000–6300	0	1.0	(34)
Iodine with ferrous ion Fe^{++} ; I^-	H_2O	I_3^-	3660–5790		1	(63)
Iodine with formate \rightarrow CO	H_2O	I_3^-	3450–3500	15–25	(26–64)	(30)
Iodoform decomposition	C_6H_6	CHI_3	3130 and 3660	16–25	(1)	Increases with oxygen (50)
Ketene decomposition C_2H_4 ; CO	Gas	CH_3CO	3130 3660		1 0.4	(100) (90)

Lead tetramethyl decomposition \rightarrow Pb; C_2H_6	Gas	$Pb(CH_3)_4$	2537	25-29	1.11	Radioactive lead used; 22-31 mm. pressure.
	$(CH_3)_3C_2H_7$	$Pb(CH_3)_4$	2537		0.37	0.0067 <i>M</i>
					0.42	0.0028 <i>M</i> (74)
Lead tetraphenyl decomposition \rightarrow Pb; $C_{12}H_{10}$	C_6H_6	$Pb(C_6H_5)_4$	2537		0.37	Radioactive lead used (74)
Malachite green leucocyanide	C_2H_5OH	Malachite green	2537-3130	26-29	1.0	Colorless to colored compound (54)
Maleic-fumaric acid isomerization	H_2O	$HCCOOH$ \parallel $HCCOOH$	2070-2820	18	(0.03)	0.01 <i>M</i> (117, 123)
			3130	18	0.05	0.01 <i>M</i> (117)
Maleic-fumaric ester isomerization	CCl_4	Br_2	4360 5460	20	300 150	Bromine-sensitized reaction accompanied by addition of bromine (35)
Mercury dimethyl decomposition \rightarrow Hg; C_2H_6 ; CH_4	Gas	$Hg(CH_3)_2$	2537	20 189	1.0 2.2	20 mm. pressure; no inhibition by nitric oxide (116)
Methane decomposition \rightarrow C_2H_6 ; H_2	Gas	CH_4	1400-1600 1295-1469	25	(1) (1.3)	Calculated from hydrogen produced (53, 75)
Methanol decomposition \rightarrow H_2 ; H_2CO	Gas	CH_3OH	1800-2000		(1)	(96)

TABLE 1—Continued

REACTION AND PRODUCTS	SOLVENT	ABSORBER	WAVE LENGTH Å	TEMPERA- TURE °C.	QUANTUM YIELD	REMARKS AND REFERENCES
Methylamine decomposition → NH ₃ ; H ₂ ; CH ₃ NCH ₃	Gas	CH ₃ NH ₂	Hg arc	100–105	<0.7	(37)
Methyl butyl ketone de- composition → (CH ₃) ₂ CO; C ₂ H ₆	Gas	CH ₃ COC ₄ H ₉	2480–2770	127	0.27	1 atm. pressure
Methyl butyl ketone poly- merization	Gas	CH ₃ COC ₄ H ₉	2480–2770	127	0.03	(13)
Methyl iodide decomposition → CH ₄ ; C ₂ H ₆ ; I ₂	Gas	CH ₃ I	Hg arc 2026	25	(0.06) <0.01	H ₂ and N ₂ O without effect (111) At 140 mm. (132)
Methyl iodide with hydriodic acid → CH ₄ ; I ₂	Gas	CH ₃ I	Hg arc		(2)	Independent of composition (59)
Methylacetylene polymeriza- tion → (CH≡CCH ₂) _n	Gas	CH≡CCH ₃	Hg arc	25	3.5	(78)
Monobromoacetic acid hy- drolysis → HOCH ₂ COOH; Br ⁻ ; H ⁺	H ₂ O	CH ₂ BrCOOH	2537		0.3	0.01 M (101)
Monochloroacetic acid hy- drolysis → HOCH ₂ COOH; Cl ⁻ ; H ⁺	H ₂ O	CH ₂ ClCOOH	2537 1850–2300		1 0.9	Affected by pH (101) (38)

Nitrate ion decomposition → NO ₂ ⁻ ; O ₂	H ₂ O	NO ₂ ⁻	2536 3130 2536	25	0.3 0.01 0.05	At pH = 10 At pH = 10 At pH = 6 (120)
Nitric oxide → N ₂ + O ₂	Gas	NO	1832		0.75	(81)
o-Nitrobenzaldehyde rear- rangement → C ₆ H ₄ (NO) COOH	Liquid Gas	C ₆ H ₄ (NO ₂)CHO	2540-3660 3500	45-75 120 120	0.5 0.8 0.5 0.5 0.5	(136) 5 mm. pressure; with N ₂ = 1 atm. (68) (73)
Nitrogen dioxide decomposi- tion → NO; O ₂	(CH ₃) ₂ CO Solid		3130-4360			
	Gas	NO ₂	4050 3660 3130	0	0.5 1.83 1.93 <0.05	Decreases regularly with in- creasing pressure of inert for- eign gas (6, 57, 88) (57)
Nitrogen tetroxide decompo- sition → NO; O ₂	CCl ₄	NO ₂	3660-4050	0		
	Gas	N ₂ O ₄	2800 2650	0	0.2 0.4	(57)
Nitrogen pentoxide decompo- sition → NO ₂ ; O ₂	Gas	N ₂ O ₅	2800 2650	0	0.6 0.6 <0.05	(57)
Nitrogen pentoxide with di- oxide → NO ₂ ; O ₂	CCl ₄ Gas	NO ₂	2650-2800 3130-4050	0 0		Results same as given under NO ₂ decomposition (57)
Nitrous oxide decomposition → N ₂ ; O ₂ ; NO	Gas	N ₂ O	Al spark		1	(93)
β-Nitroso-β, ε-dimethylhex- ane decomposition → H ₂ N ₂ O ₂ , etc.	C ₆ H ₆		6850		(1)	(4)

TABLE 1—Continued

REACTION AND PRODUCTS	SOLVENT	ABSORBER	WAVE LENGTH	TEMPERATURE	QUANTUM YIELD	REMARKS AND REFERENCES
Nitrosoisopropylacetone decomposition \rightarrow $\text{H}_2\text{N}_2\text{O}_2$, etc.	C_4H_8	$(\text{CH}_3)_2\text{C}(\text{NO})-\text{CH}_2\text{COCH}_3$	λ 6850	$^{\circ}\text{C}$.	(1)	(4)
Nitrosyl chloride decomposition \rightarrow NO ; Cl_2	Gas	NOCl	3650–6300	22	2	(64)
Oxalic acid decomposition \rightarrow H_2O ; CO ; CO_2	H_2O	Complex ion UO_2^{++} with $\text{H}_2\text{C}_2\text{O}_4$	2550 3130 3660 4350	25	0.60 0.56 0.49 0.58	Accurately known. This reaction is the universal standard for actinometry (72)
Oxalyl chloride decomposition \rightarrow COCl_2 ; CO	Gas	$(\text{COCl})_2$	2537 3660	25	0.8 1.8	(67)
Oxidation of acetone \rightarrow CO_2 ; H_2O ; CH_3COOH	Gas	$(\text{CH}_3)_2\text{CO}$	3130	25	0.24	ϕ same as for decomposition (45)
Oxidation of carbon monoxide \rightarrow CO_2	Gas	COCl_2	Hg arc		87–110 (1000)	Sensitized by phosgene. Each of three gases at 200 mm. (85) Sensitized by Cl_2 (102)
Oxidation of carbon tetrachloride \rightarrow COCl_2 ; Cl_2	Gas	Cl_2	4050–4360			
Oxidation of carbon tetrachloride \rightarrow COCl_2 ; Cl_2	Liquid	CCl_4	2537	25	1	(79)
Oxidation of chloroform \rightarrow COCl_2 ; HCl ; Cl_2	Gas	Cl_2	4360	25 65	(100) 260	Sensitized by Cl_2 (23) (106)

Oxidation of hydrogen → H_2O_2 ; H_2O ; O_2 → H_2O_2 ; H_2O ; O_2	Gas	O_2 Hg	1719-1725 2537	20	1 2.6	Varies with pressure (109) Sensitized by Hg. Corrected value of Φ (80)
Oxidation of hydrogen → H_2O_2 ; H_2O	Gas	Hg	2537	50-200	1.2	Hg-sensitized. Light intensity 100 times that of Marshall (44, 80)
Oxidation of mandelic acid	H_2O	Br_2 UO_2^{++} UO_2^{++}	3660-5460 2560-3130 2547-4360	31 27	(12.5) (31.7) (1)	Under certain conditions (46) Under certain conditions (49) For low concentration UO_2^{++} . Methylene blue present (48)
Oxidation of methylene io- dide → HCOOH ; CO ; H^+ ; I^-	Liquid	CH_2I_2	3100	21	1.4	With respect to iodine (52)
Oxidation of phosgene → CO_2 ; Cl_2	Gas	COCl_2	Hg arc		1.8	COCl_2 , 63 mm.; O_2 , 68 mm. (85)
Oxidation of phosphine → H_2O ; P_2O_5	Gas	PH_3	Zn spark	18	200	At 0.05 mm. (82)
Oxidation of quinine and its derivatives by dichromic acid	H_2O	Alkaloid	3130 3660 4050	5-24	0.065 0.070 0.027	Hydroquinone and ten other derivatives of quinine given also. Φ 's all range from 0.002 to 0.07 (41)
Oxidation of rubrene → $\text{C}_{30}\text{H}_{20}\text{O}_2$	C_6H_6 $\text{C}_6\text{H}_5\text{N}$	$\text{C}_{30}\text{H}_{20}$	4360	0-18	1	For large concentrations of rubrene and O_2 (65)

TABLE 1—*Concluded*

REACTION AND PRODUCTS	SOLVENT	ABSORBER	WAVE LENGTH	TEMPERATURE	QUANTUM YIELD	REMARKS AND REFERENCES
Oxidation of sulfur dioxide → SO ₂	Gas	SO ₂	Å 1860 2070	°C.	3.1 2.0	(66)
Oxidation of tetrachloro- ethylene → COCl ₂ ; CCl ₄ COCl	CCl ₄	Cl ₂	4360	20	1	At low concentrations (33)
Ozone formation O ₂ → O ₃	Gas	O ₂	<2000 <1750		1.3-2.0 2.0	Depending on pressure (124) (118)
Ozone decomposition → O ₂	Gas	O ₃	2080-3130 2100-2800	0-60 2-20	1.8-6.2 1.6-130	Dry ozone at 177 and 390 mm. Varies with pressure (56) In presence of moisture. De- pends on pressure (42)
Persulfate ion → SO ₄ ²⁻ ; O ₂ ; H ⁺	H ₂ O	S ₂ O ₈ ²⁻	2536-3020		1.0	(26)
Phosphine decomposition → P ₂ ; H ₂	Gas	PH ₃	.2300	20-300	0.56 0.49	For 7 cm. bulb For 2 cm. bulb (82)
Propionaldehyde decomposi- tion → C ₂ H ₄ ; CO; H ₂	Gas	C ₂ H ₅ CHO	3130	300	3 6 8	At 100 mm. At 200 mm. At 300 mm. (84)
Propionic acid → C ₂ H ₄ ; CO ₂	H ₂ O	C ₂ H ₅ COOH	1850-2300		(1)	(38)
n-Propyl iodide → I ₂ , etc.	Gas	n-C ₃ H ₇ I	2026-2610	25	0.01	At 35 mm. (131)

Isopropyl iodide \rightarrow I ₂ , etc.	Gas	iso-C ₃ H ₇ I	2026 2610	25	0.43 0.17	At 56 mm. At 26 mm. (131)
Silver oxalate decomposition \rightarrow Ag; CO ₂	Solid	Ag ₂ C ₂ O ₄	3600-5200	100	0.12	Inhibited by O ₂ (8)
<i>trans</i> -Stilbene transformation \rightarrow <i>cis</i> -stilbene	C ₆ H ₁₄	C ₆ H ₅ HC=CHC ₆ H ₅	1930 2260 2650 3020 3130		0.36 0.41 0.73 0.73 1.01	(108)

these purposes it is often unnecessary to express the results in absolute units (quantum yields).

In many cases the quantum yield varies with temperature, concentration, and intensity. Particularly in chain reactions the quantum yield may vary considerably with slight changes in the reacting system and with traces of impurities. Special conditions, such as concentration, are given in the last column of table 1. When the temperature is not given it may usually be taken as room temperature (about 20°C.). Parentheses around a quantum yield indicate a lesser degree of accuracy. When there is uncertainty regarding Φ , the original article should be consulted. The references are given in parentheses in the last column and include references to earlier investigations.

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THE NATURE OF THE PRIMARY PROCESS IN PHOTO-CHEMICAL REACTIONS¹

G. K. ROLLEFSON

Department of Chemistry, University of California, Berkeley, California

Received May 25, 1938

In the previous reports the nature of the primary action of light in photochemical reactions has been discussed in some detail. The principal developments since that time have been concerned with the determination of the products of the photodissociation processes and with the process known as predissociation. The term "predissociation" was introduced by Henri (4) in describing certain diffuse bands discovered by himself and his associates. Their choice of this name was based on their idea that these diffuse bands corresponded to excitation of the molecule to a loosely bound state in which it could dissociate readily. The present-day views are based on the picture, offered by Bonhoeffer and Farkas (2) and by Kronig (11), that the molecule in the activated state produced by the absorption of these diffuse bands undergoes a radiationless transfer to another electronic state and dissociates in a time which is short compared to the period of rotation. Such changes have been expressed graphically by Herzberg (6) by means of potential energy diagrams (figure 1). The transition from one state to another by this predissociation process must occur without any appreciable change in the separation of the atomic nuclei or in the energy of the system. From the standpoint of the diagrams, this means that we have radiationless transitions occurring only at the intersection of two curves. In our diagram (figure 1), if the excitation by light takes the molecule from the normal state, n , to a state represented by a point on the curve a above the level of the intersection of that curve with a' , then as the molecule vibrates in the excited state we have the possibility of a transfer from a to a' occurring. If this intersection point is above the level corresponding to the dissociation of the state represented by a' , the molecule will dissociate within the next vibration.

The diagrams (figure 1) must be looked upon as schematic only, since, actually, we cannot specify the positions and energies of the atoms with the precision indicated by the curves. According to Heisenberg's Uncertainty Principle, the product of the uncertainties of position and mo-

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mentum is $h/2\pi$. A more convenient form for us to use in the discussion of predissociation is that the uncertainty in the energy multiplied by the uncertainty of the time is $h/2\pi$. Our curves therefore should be looked upon as representing mean values only. Furthermore the intersections of two curves must be considered not as points but rather as regions within which the molecule may be thought of as being in an indeterminate state. The probability of a transfer occurring will depend upon the time that the molecule is in this indeterminate condition. This time will depend on the kinetic energy of vibration and the range over which the transition may occur. Thus in figure 1a we should expect the transition to occur only if the condition of the molecule corresponds to a point rather close to the intersection. On the other hand, in figure 1b, where the two curves cross at a small angle, when

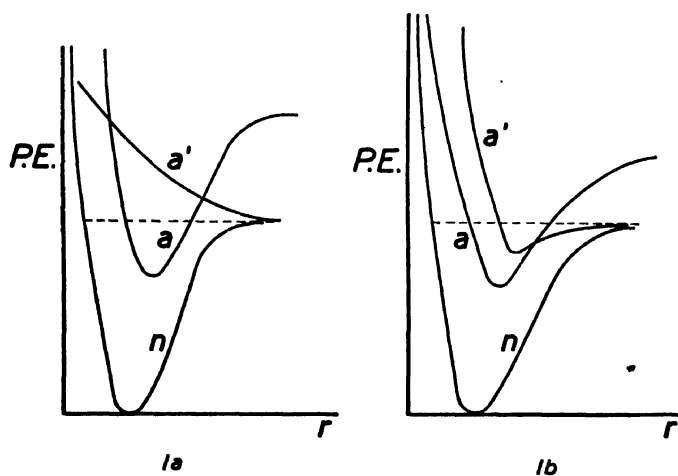
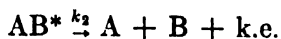


FIG. 1. Potential energy diagrams

we take into consideration the blurring called for by the Uncertainty Principle, we see that there will be a long region along the curve *a* which is in the indeterminate area. Hence we should expect, other things being equal, that molecules represented by diagrams similar to figure 1b will show predissociation over a wider range and more frequently than those corresponding to the other diagrams. At the present time we do not know enough about these potential curves to make any quantitative calculations concerning predissociation. Furthermore, these curves must be considered as only schematic for polyatomic molecules, as they are far from simple vibrators.

The Uncertainty Principle also accounts for the appearance of a diffuse spectrum. If the excited state dissociates within a time τ the width, w , of the spectrum line which put the molecule into that state will be given by

$w\tau = h/2\pi$ or, if we express w in cm.^{-1} , $w\tau = h/2\pi c$. In any ordinary spectrum which shows a fine line structure, the broadening due to the Doppler effect is ten to one hundred times the natural width of the line; therefore the predissociation process must shorten the life of the excited state by a factor of this magnitude for the effect to be noticeable. It is to be expected therefore that, whenever we find a diffuse absorption spectrum, fluorescence will either be very weak or absent. If we consider the competition between fluorescence and decomposition as represented by



the fraction of the activated molecules which radiate will be given by $\frac{1}{1 + k_2/k_1}$. Hence, the greater k_2 is relative to k_1 , i.e., the shorter the life period, the weaker will be the fluorescence. As k_2 usually must be ten to one hundred times k_1 for a diffuseness to be observed, it follows that a marked weakening of fluorescence is a more sensitive indicator of predissociation than a diffuse spectrum.

It is by no means universally true that we have transitions from one state to another occurring whenever we have a crossing of the potential energy curves for those states. Kronig (11) has set up the following selection rules for diatomic molecules: (1) There shall be no change in the total angular momentum. (2) Transitions occur only between states of the same multiplicity. (Invalid for large multiplet separations.) (3) The quantum number Λ changes by 0 or ± 1 . (4) Transitions occur from a positive to a positive state or from a negative to a negative. (5) If both atoms are the same, the states involved in a transition are either both symmetrical or both antisymmetrical. The interpretation of the spectra of polyatomic molecules has not progressed to the point where we can say whether an analogous set of rules applies or not. However, we may say that we can expect to find the probabilities of radiationless transfers occurring ranging from practically every time the molecule reaches the state represented by the intersection of the potential energy curves to practically complete prohibition of the change.

The probability of a radiationless transfer occurring is modified considerably by a magnetic field or collisions with other molecules. This gives rise to the phenomenon known as induced predissociation. Experimental evidence for the occurrence of this process was obtained by Loomis and Fuller (12) and by Kondratjew and Polak (10) in the study of the absorption spectrum of iodine. They found that the addition of inert gases increased the absorption coefficient of iodine in the vapor state for those bands involving values of ν' , the vibrational quantum number in the upper

state, greater than 12. Turner (15) found that, if iodine vapor were illuminated with light absorbed in the band region in the presence of a magnetic field or inert gases, there was a marked absorption of the spectrum lines characteristic of iodine atoms. More recently, Rabinowitch and Wood (13) have made a more quantitative study of the effect of inert gases. In their experiments, the dissociation of the iodine was determined by measuring the light absorbed by the remaining iodine molecules. They concluded that argon, nitrogen, and oxygen caused the dissociation of the activated molecule at every "gas-kinetic" collision. Helium was somewhat less effective but, with a pressure of 500 mm. of that gas, all of the molecules absorbing light were dissociated.

In the case of bromine we have some evidence that dissociation occurs in the band region even without the aid of collisions. Urmston and Badger (16) found in their experiments on the photochemical reaction of bromine with platinum that the rate of the reaction was independent of the distance between the platinum and the illuminated zone. Their experiments were performed at low pressures, so that induced predissociation did not need to be considered. Neither could their results be accounted for on the basis of active molecules, as they were unable to demonstrate that fluorescence was confined to the illuminated zone. It is possible that the reaction was due to a continuum underlying the band absorption, a situation analogous to that in the hydrogen-chlorine reaction which has been discussed recently by Bayliss (1). However, no appreciable difference was noted in rates whether blue or yellow light was used. Other reactions in which no effect was noted on comparing the rates using blue and yellow light are the bromination of acetylene (3) and the formation of hydrogen bromide (8). The effect of inert gases on the latter reaction has been studied in considerable detail. Instead of finding an accelerating effect, which could be attributed to induced predissociation, a retarding effect was noted, due to an increased rate of recombination of bromine atoms (7, 8, 14). This is understandable if we assume that with bromine, as has been found with iodine, every collision of an activated molecule results in dissociation. Under such conditions, no effect assignable to induced predissociation would be detectable above about 10 mm. pressure.

A quite different result has been reported for the hydrogen-chlorine reaction by Hertel (5). He found that, if the light absorption occurred in the banded region of the spectrum, this reaction was accelerated by the addition of inert gases. This effect was believed to be due to the activated molecules being dissociated by collisions. The mechanism of such a dissociation is probably induced predissociation.

The examples which we have just discussed show no sign of predissociation in their absorption spectra, indicating that the life of the undisturbed activated molecule is at least of the order of 10^{-9} sec.; with iodine, studies

of the fluorescence indicate a life of 10^{-7} sec. It is apparent, therefore, that spontaneous or induced predissociation may occur with any kind of light absorption. Hence, the possibility of dissociation in the primary step of a photochemical reaction cannot be excluded on the basis of well-defined lines in the absorption bands nor even on the basis of fluorescence observations.

Another interesting example is furnished by tellurium vapor, Te_2 . In this case the limits of the natural and induced predissociation do not coincide. The difference must be due to the induced effect involving a lower lying level than the spontaneous process (9).

If the light is absorbed by a complex molecule it is much more difficult to demonstrate an effect due to induced predissociation on account of the complexities introduced by secondary reactions. Usually, the photochemical experiments are carried out at such high pressures that the induced predissociation is a maximum if it is anything like that with simple molecules. Any effects of this type must therefore be sought for at low pressures, particularly in systems for which the quantum yield of the primary process is less than 1.

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SOME COMPARISONS BETWEEN PHOTOCHEMICAL PROCESSES IN GASES AND SOLUTIONS^{1,2}

ROSCOE G. DICKINSON

Department of Chemistry, California Institute of Technology, Pasadena, California

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The chief purpose of the present section of this report is a comparison of photochemical reactions in the gaseous state with those in solution or in the liquid state. It is not proposed to enter into a detailed discussion of photochemical processes in solution but rather to indicate the relation of such processes, when possible, to those occurring in the gaseous state. This section accordingly contains a brief statement of viewpoints involved in comparing gaseous and solution or liquid reaction, together with some discussion of pertinent experimental results.

In recent years theories of the liquid state and of various phenomena occurring in liquids have undergone active development; this may, for example, be seen in the general discussion of the liquid state published by the Faraday Society (43) as well as in other papers to which specific reference will be made. Theoretical approaches to the liquid state have sometimes started with the gaseous state and have sometimes started with the crystalline state; Bernal (4), however, has given reasons for believing that liquid structure, while having points of close resemblance to the crystalline, is of a character that can not be reached by continuous transition from the crystalline state.

Current views are that a liquid, at not too high a temperature, aside from differing from a gas in the matter of coherence, possesses a somewhat quasi-crystalline structure. This does not necessarily show itself in any large regions with crystalline regularity but appears rather in the character of the distribution function $p(r)$, where $4\pi r^2 p(r) dr$ gives the probability of finding a second molecule within the distance range r to $r + dr$ of a chosen molecule. This distribution function has been investigated by x-ray diffraction methods (25, 42, 5, 11, 29) and by experiments with models (30). The function does not show the monotonic character expected for a dilute gas, but rather exhibits maxima and minima which

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become less pronounced with increasing r but are evident for a distance of several molecular diameters. The structure, at least in the case of simple non-polar liquids, may be thought of as such that a chosen molecule has immediately coördinated about it a number of other molecules at a distance corresponding to the first maximum of $p(r)$, others more loosely coördinated at a distance corresponding to the next maximum, and so on. The chosen molecule is accordingly closely confined in a "cage" of surrounding molecules, so that its motion becomes in part a pseudo-oscillatory one within this cage. (One estimate (8) places the mean displacement between the extremes of oscillation at about 0.5 Å.) This suggests that, for diffusion to occur, the molecule must acquire sufficient energy to break through the wall of immediately surrounding molecules (8), i.e., to move to the center of a new coördination complex (33).

In calculating numbers of collisions of solute molecules with each other, the custom has been to treat the solute as if it were gaseous with solvent absent; in the calculation the molecules have been ordinarily regarded as rigid. In recent theories the occurrence of collisions has been modified both as to distribution in time and as to average number per unit time. In view of the cage effect of the solvent molecules, once two solute molecules have made collision there is a greater probability of further collision between the same pair than would be the case in a gas. Thus a given solute molecule undergoes collisions with other solute molecules in sets. The occurrence of such collision sets has been found in experiments with models (35). For thermal bimolecular reactions between solutes, the number of sets per unit time is important when there is high probability of reaction at any collision, but the total number of collisions per unit time rather than the number of sets becomes important when any considerable activation energy is required (8, 33, 46). Present estimates of the total collisions per unit time between solute molecules give values rather higher (five to twenty times) than those from a gas calculation. In view of the present state of flux in these ideas, it would be premature to recommend any one mode of calculating collision numbers.

Specific information concerning primary absorption processes is considerably more abundant and certain for gaseous substances than for substances in the liquid state or in solution. This arises partly from the relative simplicity of the phenomenon in the gaseous state, where the absorption is by fairly isolated molecules, and partly from the related fact that in condensed states the fine structure of absorption spectra is lost, together with the detailed information derivable from such structure. Aside from the smoothing out of fine structure into a continuum in solution, dissolved substances frequently show spectra differing from those of the same substances in the gaseous state, both as to magnitude of absorption coefficient and as to position of absorption maxima. This is not

surprising, since solution may be accompanied by such processes as solvation, dissociation, or ionization producing essentially new absorbing molecules. However, when interactions between molecules in the solution are not too great, the solution absorption spectrum becomes essentially a blurred copy of that of the gas. For example, the absorption coefficients of the halogens in non-polar solvents such as carbon tetrachloride differ little from values for the gases. In cases where this close similarity exists, it is usual to presume that absorption is accompanied by the same electronic transition in both cases, and to draw inferences concerning the primary process in solution from a knowledge of that in the gas.

When a molecule in solution absorbs a quantum of radiation, there is initially produced an excited molecule for which there exists a variety of conceivable fates. Among these are the following: The molecule may (a) immediately lose its excitation energy through collision of the second kind with solvent molecules, whereby the absorbed energy becomes ineffectively distributed through the solution, or it may (b) retain its excitation (in part at least) in spite of collisions with the solvent molecules and later fluoresce or enter into reaction; again, (c) the absorbing molecule may immediately enter into chemical reaction with an adjacent solvent molecule; and finally, (d) the molecule, after a lapse of time possibly dependent on whether a true continuous or a predissociation spectrum is involved, may dissociate.

Since molecules in solution are practically continuously in the process of collision with solvent, the effect of collisions of the second kind in degrading activation energy from light absorption may be expected to be of greater importance in solution than in the gaseous state. Indeed, the ability of a molecule to retain its excitation in solution sufficiently to fluoresce or to react with a second molecule of solute implies a considerable insensitiveness toward collisions of the second kind. Among inorganic substances only a few, such as the uranyl salts and compounds of the rare earths, are known to fluoresce in solution; among organic substances the phenomenon is largely confined to various ring compounds. The view has been that, in substances showing fluorescence in solution, the electronic transition was one protected from outside influences either because of occurring in the interior of an atom or because of occurring in a protected part of a complicated molecule. Frank and Levi (17) have remarked that this view is incomplete and does not explain how some substances may fluoresce yet have their fluorescence strongly suppressed by the addition of various substances to the solution. Using the idea that the electronic excitation energy of the absorbing molecule can be easily transformed only when it is approximately equal to that of a new electronic state (of the absorbing molecule, the collision partner, or both), Franck and Levi have discussed the conditions for fluorescence, quenching, and reaction in terms of potential energy curves. The retention of electronic excitation permitting

reaction with a second molecule of solute is probably somewhat exceptional, most photochemical reactions occurring as a result of reaction with the solvent or of the formation of atoms or free radicals. In connection with these considerations, attention should be given to cases where sensitization of solute reaction by the solvent occurs. In the conversion of *o*-nitrobenzaldehyde into *o*-nitrosobenzoic acid in acetone solution (45), the gross quantum yield (molecules transformed per quantum absorbed by the system) for 3130 Å. remains near 0.5 for acetone solutions containing from 2 per cent to 0.02 per cent of aldehyde, although, at the lower concentration, 96 per cent of the absorption is due to the acetone. Again, the decomposition of ethyl iodide at a mean wave length of 2610 Å. gives a quantum yield (48) in 0.03 molar solution in benzene of 0.52, although only 1/180 of the absorption is due to the ethyl iodide; moreover in hexane solution, where the absorption is all due to the ethyl iodide, the yield is substantially the same. The mechanisms of these sensitizations are not known.

If, in the gaseous state, an induced predissociation occurs in competition with fluorescence, then, in solution, the dissociation may evidently be favored. However, even if the molecule does dissociate, there exists a possibility that the dissociating partners, in view of the fact that they are closely hemmed in by solvent molecules, will frequently immediately recombine. The greatly increased probability of this occurrence in solution has been emphasized by Franck and Rabinowitsch (18); they have called the process "primary recombination" to distinguish it from the "normal" recombination process which involves the uniting of atoms or radicals which were not previously partners. It has long been recognized that the Einstein photochemical equivalence law does not, in general, apply to the overall photochemical reaction, but frequently only to the primary process. The effect of a dissipation accompanying the absorption, or of primary recombination, would operate to prevent the occurrence of an integral relationship between the number of quanta absorbed and the number of *primary* products of the absorption process.

Existing experimental evidence which might be expected to have a bearing on the question of primary recombination may for the most part be divided into three classes: (1) experiments in which the stationary concentration of the primary products of dissociation is estimated by measurement of the light transmission of the solution while under irradiation; (2) photochemical experiments in which a reaction proceeds by a chain, with the rate of reaction interpreted as depending on the stationary concentration of transient substances resulting from the absorption process; and (3) photochemical experiments in which no chain is presumed to be involved and in which the stationary concentrations of transients are of secondary interest.

Extensive experiments of the first type have been carried out by Rabino-witsch, Wood, and Lehmann. In these the stationary decrease in concentration of halogen molecules under a measured strong irradiation was determined. With iodine in carbon tetrachloride or hexane solution (34), the processes apparently involved were only the photodissociation of the molecules and recombination of the atoms. If the fraction β of absorbed photons gives dissociation



so that the rate of production of atoms by dissociation is $2\beta(I_{\text{abs.}})$, and if the atoms disappear only by recombination $2\text{I} \rightarrow \text{I}_2$ with a rate $2k(\text{I})^2$, the value of β is evidently given by

$$\beta = k(\text{I})^2/(I_{\text{abs.}})$$

at the steady state. Corresponding values of (I) and $(I_{\text{abs.}})$ have been measured experimentally; the value derived for β then depends on what is assumed concerning k . If a pair of normally diffusing iodine atoms are assumed to combine on their first collision, and if it be assumed that the specific rate, Z , of such collisions may be calculated with the gas kinetic expression

$$Z = 2\sqrt{\pi}d^2\sqrt{RT/M}$$

then this specific collision rate may be set equal to k and β may be obtained. Taking $d = 5.0 \times 10^{-8}$ cm., the data lead to average values of β of 0.7 ± 0.3 for I_2 in carbon tetrachloride and 1.0 ± 0.3 in hexane. However, if in the absence of combination, collisions between normally diffusing iodine atoms were to occur in sets of, on the average, n collisions each, then, with combination at the first collision, k becomes Z/n and the calculated values of β become the former values multiplied by $1/n$. Again if, in accord with ideas mentioned earlier, the total number of collisions between solute molecules is somewhat greater than the value given by the gas formula, say m times that value, then the calculated values of β become m/n times the values given above. Thus, while values of β of the order of magnitude of unity are compatible with the experimental results, more definite independent knowledge of the recombination rate is necessary in order to make a definite determination of β from the stationary concentrations.

The assumption that two particles just leaving a photodissociation have the same probability of immediate collision as two particles leaving an ordinary collision is doubtful when (as is usually the case) the dissociating partners have considerable excess kinetic energy. Rollefson and Libby (36) have urged that "such atoms have an excellent chance of forcing their way between the solvent molecules" so that the two probabilities would

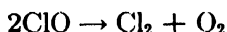
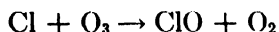
not be equal. Rabinowitsch and Wood (35) had considered such a dissymmetry of cage effect possible when the molecules of the solvent were smaller in mass than the dissociation products but not when the solvent was greater since, from conservation of momentum, the dissociating products would be brought to rest by their first collision with the heavier particle irrespective of their kinetic energy. However, this consideration applies primarily to head-on collisions and may not seriously affect the contentions of Rollefson and Libby. In this connection it may be remarked that activation energies for diffusion of 3000 cal. and less have been calculated (8); at least this excess is often possessed by dissociating partners in photochemical experiments.

If it be admitted that the probability of separation is greater for a pair of photodissociating atoms than for a pair in normal collision, then an effect of wave length on stationary concentrations becomes possible. Such an effect was sought (34) but not certainly found.

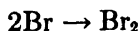
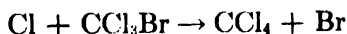
Turning now to photochemical evidence concerning primary recombination, there are various photochemical chain reactions to which mechanisms have been assigned which are such that the rate of reaction is proportional to the steady concentration of transients produced immediately or indirectly by the light absorption process. Simple examples are the sensitized decomposition of ethylene iodide and the iodine-sensitized transformations of geometrical isomers. Attempts to draw inferences concerning primary recombination from the rates of such reactions encounter the same ambiguities, *inter alia*, as discussed above in connection with the experiments of Rabinowitsch and Wood. However, here again, if the solvent effect is not the same for primary and secondary recombination, a wave length effect is possible; for, whereas the secondary recombination is presumably unaffected by wave length, the kinetic energy of the dissociating partners will be smaller at longer wave lengths with possibly more primary recombination and a smaller rate of reaction. Reactions of the type under discussion often proceed at rates proportional to the square root of the intensity of illumination. In such cases the total material reacting per unit time depends not only on the rate of absorption of radiation but on the distribution of absorption through the reacting medium (1); this point has, unfortunately, been frequently ignored. A rather small wave length effect has been reported (14) for the iodine-sensitized ethylene iodide decomposition; the primary quantum yields for the wave lengths 4358, 5461, and 5780 Å. were found to stand in the ratios 1:0.87:0.75. Other halogen chain reactions in which yields somewhat smaller at longer wave lengths than at shorter have been reported are the following: the bromination of cinnamic acid in carbon tetrachloride solution (2); the bromination of liquid benzene (32); the bromination of maleic ester and its sensitized rearrangement to fumaric ester (15); the iodination of various olefins in

chloroform solution at -55°C . (16). It is to be noted that similar wave length effects have been reported absent in the following *gaseous* reactions: the formation of hydrogen bromide (22); the bromination of acetylene (6); the bromination of cyclohexane (23); the bromine-sensitized decomposition of chlorine dioxide (40, 41). Considerable wave length effects in the same sense are often found in aqueous solution reactions, but caution must be exercised in attributing them to varying primary recombinations as opposed, for example, to reaction with solvent or to the occurrence of different electronic transitions on absorption.

The situation can be somewhat different in the case of certain reaction mechanisms not involving a chain. If conditions are such that the atoms or radicals formed in the primary process always react with some solute to give products without the intervention of a chain, then the gross quantum yield may be used to give indications of the primary quantum yield. A necessary experimental condition is evidently a constancy of gross quantum yield over a range of concentrations of reactant. Reactions which may be of this type have not been very thoroughly examined. The decomposition of ozone in carbon tetrachloride solution sensitized by chlorine has been reported (7) to occur with a quantum yield of 2O_3 decomposed per quantum absorbed at the wave length 3660 \AA . If the mechanism be such as the following (38),



the observed quantum yield would indicate absence of primary recombination. The gaseous reaction is complicated (21). Again the chlorination of trichlorobromomethane in carbon tetrachloride was reported (20) to proceed with a yield of 0.9 mole of bromine per quantum absorbed (wave lengths); if the mechanism is the following (38),



the quantum yield indicates little primary recombination. However, the compound BrCl was not known and its formation not considered in these experiments. In the gaseous reaction, chains have been found (44). The oxidation of carbon tetrachloride to phosgene by dissolved oxygen brought about by radiation (2537 \AA .) absorbed by the carbon tetrachloride has been reported (28) to occur with a yield of 1 mole of carbon tetrachloride oxidized per quantum absorbed. But in the absence of dissolved oxygen

the quantum yield of decomposition of carbon tetrachloride was found to be less than 0.01. Taken together, these results could mean either (1) no primary recombination but a low specific rate for the reaction $2\text{CCl}_3 \rightarrow \text{C}_2\text{Cl}_6$ as compared with reactions leading to reformation of carbon tetrachloride or (2) large primary recombination with a long chain oxidation. The second possibility would make the apparently simple yield of oxidation fortuitous. A similar result has been obtained (48) in the oxidation of ethyl iodide by oxygen in solution under the influence of radiation absorbed by the ethyl iodide. In the presence of oxygen a 1.38 molar solution of ethyl iodide in hexane irradiated with a wave length of 2610 Å. yielded "exactly 2 atoms of iodine for every quantum absorbed." In the absence of oxygen the yield was only 0.58. Franck and Rabinowitsch (18) pointed out how primary recombination might fail to operate through reaction of the dissociating molecule with the solvent. With the aid of radioactive chlorine Rollefson and Libby (36) have shown that, when chlorine absorbs visible radiation in carbon tetrachloride solution, little if any reaction with the solvent occurs.

A possibility of obtaining further information concerning primary recombination, that does not seem to have been exploited, is offered by the photochemical intermittency effect. To illustrate this possibility, suppose a photochemical solution reaction to proceed with the mechanism:



This mechanism involves the same processes as those occurring in the experiments of Rabinowitsch and Wood (34), and, in addition, an iodine atom catalysis of the conversion of A into B. The steady-state rate of this process is evidently $k_2\sqrt{\beta(I_{\text{abs.}})}/k$, where β and k have their former significance. If, however, the illumination is not steady but is carried out in regularly spaced periods of light and dark of measured duration, then it can be shown³ that for the measurable reaction $\text{A} \rightarrow \text{B}$, the ratio of the

³ Complete details are too lengthy to be given here. However, the considerations are simply as follows: that in the light

$$\frac{d(\text{I})}{dt} = 2\beta(I_{\text{abs.}}) - 2k(\text{I})^2$$

that in the dark

$$\frac{d(\text{I})}{dt} = -2k(\text{I})^2$$

and that at all times

$$\frac{d(\text{A})}{dt} = -k_2(\text{I})(\text{A})$$

rate under steady illumination to that under intermittent illumination is given by a complicated but known function of the measurable quantities ($I_{\text{abs.}}$), τ_{light} and τ_{dark} (the periods of light and dark in the intermittency experiment) and the unknown quantity βk . The points of importance are that, in the theory of the intermittency effect, the product of β and k occurs and may be rendered measurable by absolute measurements of ($I_{\text{abs.}}$), whereas steady-state experiments involve the ratio of β to k ; combination of results from both types of experiment may thus give β and k separately.

The idea of primary recombination has been employed (31) to account for some of the special complications arising in the decomposition of ketones in hydrocarbon solvents where reaction with the solvent occurs. It has also been employed in the discussion (47) of the decomposition of ethyl iodide, which occurs with a larger quantum yield in the liquid state than in the gaseous, and in a discussion (12) of the decomposition of ethylene iodide in carbon tetrachloride solution.

When a comparison of gaseous and solution photochemical reactions with respect to processes subsequent to the primary one is undertaken, the ordinary problems of chemical kinetics of thermal reactions are encountered. The literature on the effect of solvent on thermal reaction rate is, of course, large (see, for example, the symposium on the kinetics of reaction (10)). There are, however, two very simple ways in which the kinetics may undergo large apparent alteration in passing from the gas to even an inert solvent. If the gaseous reaction involves some wall reaction (for example, a chain-breaking step) this process will hardly occur in solution; the kinetics (including, for example, the dependence on light intensity) may then be considerably altered. If the gaseous reaction involves a three-body combination of two atoms or simple radicals, this process can be strongly favored in solution, owing to the abundant supply of third bodies by the solvent; if the combining bodies are sufficiently complicated, however, a third body is of little advantage (24).

In 1935, a collection was made (13) of photochemical reactions which had been examined in both the gaseous and the liquid or solution states. It was found that when the same reaction occurred in the gaseous state as in the liquid or in an inert solvent, the reaction was usually as fast or faster in the gaseous state. Additional cases for which this is true are the bromination of dichloroethylene (19), the chlorination of chloroform (9, 37, 39, 3), and the conversion of *o*-nitrobenzaldehyde into *o*-nitrosobenzoic acid (45, 26, 27).

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THE MECHANISM OF ALDEHYDE AND KETONE PHOTOLYSIS¹

PHILIP A. LEIGHTON

Department of Chemistry, Stanford University, California

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I. ABSORPTION SPECTRA

All aldehydes and ketones show an absorption band in the near ultra-violet, extending roughly from about 3500 Å. to below 2500 Å., absorption in which probably produces transitions in non-bonding electrons of the carbonyl group (27, 45). The band shows, in general, the common phenomenon of structure at longer wave lengths, changing to a continuum at shorter wave lengths (9, 12, 13, 14, 16, 17, 18, 19, 25, 33, 53). Only in the case of formaldehyde has rotational structure been definitely observed and, except for formaldehyde, the transition from structure to continuum is very gradual. In the lighter aldehydes there appears to be a region of diffuse bands or predissociation preceding the continuum and, in addition, the bands themselves appear to be underlaid with a continuum which gradually becomes stronger as wave length is decreased.

Fluorescence, where observed, is most intense for absorption in the long wave length part of the band, but the observed limits of fluorescence do not necessarily agree with the observed limits of structure in absorption (14, 18, 19, 53). The structure becomes less marked with increase in magnitude of the hydrocarbon residue, while among the three classes, ketones, saturated aldehydes, and unsaturated aldehydes, it is interesting to note that ketones show the least structure but the most fluorescence, while the unsaturated aldehydes show the most structure and the least fluorescence.

A second and much stronger region of absorption begins at about 2000 Å. (2300 Å. for unsaturated aldehydes). In those cases which have been investigated this is found to consist of series of either diffuse or discrete bands (49, 53), some of which fit a Rydberg formula (36). The bands are underlaid with faint continuous absorption and are followed at still shorter wave lengths (<1500 Å.) by a strong continuum (14). Photochemical investigations have been confined almost entirely to the near ultraviolet

¹ Contribution No. 5 to the Third Report of the Committee on Photochemistry, National Research Council.

region, absorption in which produces two reactions,—decomposition and polymerization.

II. THE PRIMARY PROCESS IN DECOMPOSITION

Discrete bands together with fluorescence indicate the production of a relatively long-lived molecule on absorption at longer wave lengths, while the appearance of diffuse bands and continua indicate a dissociation process at shorter wave lengths, although, as the different types of absorption overlap, the resulting processes must also overlap.

The observation that the gaseous products of photolysis in the case of the lighter aldehydes and ketones consist chiefly of carbon monoxide and hydrocarbons or hydrogen has led to the conclusion that the bond or bonds adjacent to the carbonyl group are dissociated as the result of absorption. Supporting this are energetic considerations (51) and the demonstration by Pearson and his collaborators of the production of free methyl radicals during the photolysis of acetone and, to a lesser extent, of acetaldehyde (43) as well as of ethyl, propyl, and butyl radicals during the photolyses of diethyl and higher ketones (42, 44).

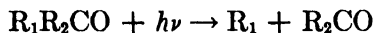
Referring to photolysis through the breaking of bonds adjacent to the carbonyl group as type I, three primary processes appear energetically possible (28):

(A) A dissociation into hydrocarbon (or hydrogen in the case of formaldehyde) and carbon monoxide molecules in one step:



where R_1, R_2 = an alkyl radical or a hydrogen atom.

(B) The dissociation of a single $R-C$ bond to produce an alkyl and an acyl radical:



(C) The dissociation of both $R-C$ bonds simultaneously to give the corresponding radicals and normal ($^1\Sigma$) carbon monoxide:



The decision as to the relative importance of these different dissociation processes constitutes one of the present problems in the photochemistry of aldehydes and ketones. The fact that aldehydes, $RCHO$, give predominantly a single hydrocarbon of composition RH , while mixed ketones give a mixture of three hydrocarbons R_1R_1 , R_1R_2 , and R_2R_2 , led Norrish and Kirkbride (34) to the conclusion that the primary process is represented by process A for aldehydes and process C for ketones. More recent observations, however, necessitate the modification of both of these suggestions.

The isolation of diacetyl by Barak and Style (4), the demonstration by

Spence and Wild (50) that, for absorption in the continuum, the C_2H_6/CO ratio in the product gas is considerably greater than unity, and that the difference is quantitatively accounted for by diacetyl formation, and the detection by Glazebrook and Pearson (15) of acetyl radicals in concentration comparable to that of methyl radicals, all resulting from the photolysis of acetone at room temperatures, is convincing evidence that process B, rather than process C, must be concerned in ketone photolysis, at least in the case of acetone. The production of hydrogen (7, 24, 26), as well as of alkyl radicals (41, 42, 43, 44), and the existence of a chain at higher temperatures (1, 21, 26) all indicate that process B or process C must be concerned to some extent in aldehyde photolysis. The low stationary concentration of atomic hydrogen compared to that of methyl radicals (11, 40) is an indication that this dissociation occurs by process B, with the splitting of the C—C rather than the H—C bond, but the existing evidence is inconclusive in this regard.

The quantum yield of decomposition of the aldehydes at temperatures below 100°C. has been found to increase with decreasing wave length in all cases studied except that of formaldehyde (24, 25, 26, 35). Accompanying the increase in quantum yield is a marked increase in the yield of hydrogen (7, 24, 26). These facts have been explained by Rollefson (48) on the basis of a competition, following absorption, between four possible paths which determine the fate of the activated molecule: (1) deactivation by fluorescence or collision, (2) dissociation into hydrocarbon and carbon monoxide by process A, (3) dissociation into radicals by process B or process C, and (4) reaction with another molecule or molecules to form a polymer. At longer wave lengths, or in the region of banded absorption, processes 1 and 4 are predominant; with decreasing wave length, in agreement with the disappearance of structure and fluorescence, processes 2 and 3 become the more important, with 3 increasing more rapidly than 2. Rollefson estimates in the case of acetaldehyde that at 3130 Å., 90 per cent of the molecules dissociating do so by process 2 and 10 per cent by process 3, while at 2537 Å. 75 per cent dissociate by process 2 and 25 per cent by process 3. The probability of dissociation into finished molecules compared to that of dissociation into radicals is thus 9:1 at 3130 Å., decreasing to 3:1 at 2537 Å. Although the magnitude of these ratios depends upon arbitrary assumptions as to the rates of the secondary reactions (26), the predominance of the dissociation into finished molecules, particularly at longer wave lengths, is in accordance with the smaller number of methyl radicals produced in acetaldehyde as compared with acetone (43), the small number of hydrogen atoms produced by absorption in the predissociation region as compared with the continuum in formaldehyde (39), and with the observation of Norrish and Bamford (30, 32) that, except as there is a reaction with the solvent, for dipropyl ketone type I photolysis is almost

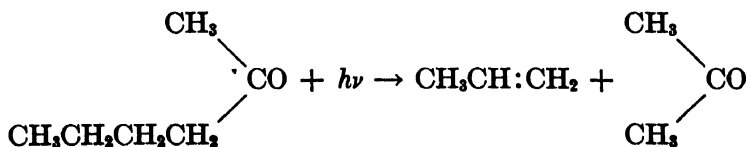
completely inhibited in solution (owing presumably to primary recombination of the radicals produced), while for isovaleraldehyde the solvent has relatively little effect. On the other hand, the report of Bowen and de la Praudiere (10) that the photolysis of acetaldehyde to yield gaseous products is virtually completely inhibited in the pure liquid would indicate a dissociation into radicals as predominant, while the statement of Akeroyd and Norrish (1) that, in the chain photolysis of acetaldehyde in the presence of acetone, it makes little difference which of these substances absorbs the light, suggests that dissociation into radicals is as efficient a process for acetaldehyde as for acetone.

Little evidence is available as to whether A and B are distinct processes (48), or whether process A results from a rapid secondary reaction following process B (7), *viz.*,



In the former case the increase in B with decreasing wave length would arise from the changing potential energy of the excited molecule and the resultant change in relative probability of transition into different unstable states; in the latter case, it would arise from a more rapid separation of the radicals with increasing energy absorbed, with resultant change in the secondary reactions. By extending the latter point of view the data thus far discussed are capable of explanation entirely on the basis of a primary dissociation into free radicals, followed by appropriate secondary reactions (8, 20). Thus, while the production of some carbon monoxide and a hydrocarbon in the initial act more readily accounts for certain features of these reactions, there appears to be no fact which definitely requires such an act as a separate primary process.

When studying the photolysis of methyl butyl ketone, Norrish and Appleyard (31) found that an entirely different type of decomposition occurred, which can best be described as a species of cracking the hydrocarbon chain:



Similar reactions, as judged from the decomposition products, have since been observed for a number of aldehydes and ketones containing an alkyl chain of three or more carbon atoms (3, 26, 29). In each case the bond between the carbon atoms α and β to the carbonyl group is broken, and a hydrogen atom or proton migrates to the α -carbon atom, leaving an olefin hydrocarbon and forming acetaldehyde or a methyl ketone. Following a suggestion of Norrish, this mode of decomposition may be referred to as

type II. Judging from the data in table 1, type II decreases in importance with decreasing wave length, but increases in importance with increasing length of the hydrocarbon chain.

Evidence that type II dissociation results in finished molecules is furnished by the observation of Glazebrook and Pearson (15) that free radicals are apparently produced only by type I decomposition, and by the fact that, in all cases, type II decomposition occurs without modification in solution (29, 32). As suggested by Norrish, it appears that this is a true primary process involving some type of resonance between the excited carbonyl group and the α, β C—C bond.

TABLE 1

Relative numbers of molecules decomposing by type I and type II photolyses, as determined by the composition of the products

COMPOUND	CONDITIONS	TYPE I	TYPE II
		per cent	per cent
<i>n</i> -Butyraldehyde.....	3130 Å.; 30°C.	90	10
	2654 Å.; 30°C.	97	3
	2537 Å.; 30°C.	100	0
Isovaleraldehyde.....	Full radiation of Hg arc; approximately room temperature	47	53
Dipropyl ketone.....	Full radiation of Hg arc; approximately room temperature	37	63
Methyl butyl ketone.....	2770-2480 Å.; 127°C.	13	87

III. SECONDARY REACTIONS IN DECOMPOSITION

That a chain reaction follows the photodissociation of acetaldehyde was demonstrated by Leermakers (21), who found that the quantum yield increases from less than unity at room temperature to values of 100 or more at temperatures around 300°C. A similar increase has been observed for formaldehyde (1); it is less marked for the butyraldehydes (26) and absent for valeraldehyde (21, 23).

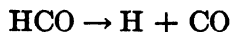
For acetaldehyde, in the temperature region of long chains, the variation in yield with pressure and intensity is given by the equation, after Leermakers,

$$-\frac{d(\text{CH}_3\text{CHO})}{dt} = k_1 I_{\text{abs.}} + k_2 I_{\text{abs.}}^{1/2} (\text{CH}_3\text{CHO}) \quad (1)$$

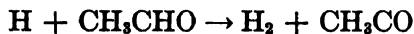
Taking into account the demonstration by Allen and Sickman (2) that methyl radicals initiate a chain decomposition of acetaldehyde, Leermakers

proposed a mechanism for the photolysis similar to that of Rice and Herzfeld (46) for the thermal decomposition (table 2).

Reaction a2 was divided into steps



and



by Leermakers and by Akeroyd and Norrish (1). The lack of a carbon monoxide deficiency in the products favors this division; the low atomic hydrogen concentration during the reaction and the greater energetic stability of formyl radicals as compared with acetyl radicals do not. Reaction a7 was included by Leermakers to explain certain differences between his work and that of Allen and Sickman, but Akeroyd and Norrish

TABLE 2

Reactions following dissociation into free radicals of acetaldehyde and acetone

a. ACETALDEHYDE		b. ACETONE	
(a1)	$\text{CH}_3\text{CHO} + h\nu \rightarrow \text{CH}_3 + \text{HCO}$	$(\text{CH}_3)_2\text{CO} + h\nu \rightarrow \text{CH}_3 + \text{CH}_2\text{CO}$	(b1)
(a2)	$\text{HCO} + \text{CH}_3\text{CHO} \rightarrow \text{H}_2 + \text{CO} + \text{CH}_3\text{CO}$		
(a3)	$\text{CH}_3 + \text{CH}_3\text{CHO} \rightarrow \text{CH}_4 + \text{CH}_3\text{CO}$	$\text{CH}_3 + (\text{CH}_3)_2\text{CO} \rightarrow \text{CH}_4 + \text{CH}_3\text{COCH}_3$	(b3)
(a4)	$\text{CH}_3\text{CO} + \text{M} \rightarrow \text{CH}_3 + \text{CO} + \text{M}$		(b4)
(a5)	$2\text{CH}_3\text{CO} \rightarrow (\text{CH}_3\text{CO})_2$		(b5)
(a6)	$2\text{CH}_3 \rightarrow \text{C}_2\text{H}_6$		(b6)
(a7)	$\text{HCO} + \text{CH}_3\text{CHO} \rightarrow \text{CH}_4 + \text{CO} + \text{HCO}$		
(a8)	$\text{CH}_3 + \text{HCO} \rightarrow \text{CH}_4 + \text{CO}$	$\text{CH}_3 + \text{CH}_2\text{CO} \rightarrow \text{C}_2\text{H}_5 + \text{CO}$	(b8)

prefer to eliminate this step. In any case, a rate law in agreement with equation 1 is obtained. Eliminating reaction a7, temperature coefficients of the photolyses of formaldehyde and acetaldehyde assign activation energies of 16 Cal. to reaction a2 and 10 Cal. to reaction a3 (1).

Recent analyses of Blacet and Volman (8) show that at room temperatures the gaseous products of acetaldehyde photolysis consist entirely of hydrogen, methane, and carbon monoxide, with no ethane or ethylene. The H_2/CO ratio decreases toward zero with increasing wave length and increasing temperature above 30°C. and with decreasing temperature below 30°C.; it decreases but slightly with increasing pressure. These results are in accordance with the Leermakers mechanism provided that reaction a5 serves as the chief chain-breaking step at low temperatures, and indicate that, contrary to Leermakers' conclusion, reaction a3 is still effective even at room temperature.

Contrasting sharply with the aldehydes, the quantum yield of acetone decomposition remains at unity or less even up to 400°C. (1, 22). At room temperature the sole products in quantity, as demonstrated by Spence

and Wild (50), are diacetyl, ethane, and carbon monoxide. With increasing temperature the yield of diacetyl decreases, disappearing entirely above 60°C., although diacetyl itself is stable at this temperature, while in the gaseous products the C_2H_6/CO ratio approaches unity and considerable quantities of methane appear. For absorption in the continuum ($< 2900 \text{ \AA.}$) at room temperature, the C_2H_6/CO ratio increases with acetone pressure and with light intensity, approaching a constant value at high intensities. At 60°C., also for absorption in the continuum, the yield of methane increases with increasing acetone pressure and with decreasing intensity. These data may be accounted for on the basis of Rice and Herzfeld's thermal decomposition scheme (46, 47), as later applied by Leermakers (22) and Patat (38) to the high-temperature photolysis of acetone (table 2).

The analytical data of Spence and Wild are explained by an increase in importance of reactions b3 and b4 with increasing temperature. At 20°C. reaction b3 is negligible, while the observed C_2H_6/CO ratio of 1.6 to 2.5 means that from 50 to 75 per cent of the acetyl radicals are reacting by reaction b5 to form diacetyl. At 60°C. absence of diacetyl indicates that the acetyl radicals are reacting entirely by reaction b4, while the amount of methane produced shows that from 15 to 40 per cent (depending on light intensity and pressure) of the methyl radicals are reacting by reaction b3. The thermal stability at room temperature and the instability at slightly higher temperatures, which are thus indicated for acetyl radicals, are verified by the report of Glazebrook and Pearson (15) that these radicals may be detected during the photolysis at room temperature but not at 60°C.

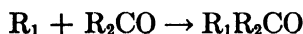
The absence of a chain in acetone photolysis signifies that the CH_3COCH_3 radicals produced by reaction b3 are incapable of further reaction with the acetone. Their ultimate fate is unknown. This mechanism is in harmony with Glazebrook and Pearson's observation that methyl radicals yield no diacetyl with acetone, and with the observation of Akeroyd and Norrish that, in acetone-acetaldehyde mixtures, there is neither inhibition or sensitization of the photodecomposition of one substance by the other, and that it makes little difference which compound absorbs the light.

The importance of reaction b5 at room temperatures in the acetone decomposition justifies its inclusion as the chain-breaking step in the low-temperature aldehyde photolysis. With the increase in rate of reaction 4 at higher temperatures, reaction 5 disappears and reaction 6 presumably becomes the chain-breaking step. Reaction b8 was considered necessary by Spence and Wild to account for the approach to a constant C_2H_6/CO ratio at high intensities. The absence of ethane in the decomposition products of acetaldehyde (8) shows that reaction b8 is negligible in acetaldehyde photolysis.

In the discussion thus far, no means have been provided to account for

the low quantum yields, particularly of acetone and of the unsaturated aldehydes. The decomposition yields of crotonaldehyde and of acrolein are below 0.04 at room temperature (5, 6). Although no direct measurements appear to have been made of the quantum yield of acetone photolysis below 56°C., at this temperature, with an incident intensity of $\sim 10^4$ ergs cm.⁻² sec.⁻¹ of 3130 Å., it varies from 0.17 at atmospheric pressure to 0.04 at 50 to 80 mm. of acetone (12). These values were calculated on the basis of pressure change with the assumption of two molecules of gas per molecule decomposed. That the yield is much lower at room temperature is indicated by the observation of Taylor and Jungers (52) that the rate of carbon monoxide evolution from acetone at ~ 80 mm. in the presence of ethylene at 150 mm. and exposed to the full radiation of a hot mercury arc is only one-tenth as great at 25°C. as at 80°C.

Four means of accounting for these low yields have been proposed: (a) The primary yield is unity, but the overall yield is reduced by a recombination of radicals (6, 20, 24), c.g.,



where R_2 = a hydrogen atom or an alkyl group. (b) A reorganization or distribution of the absorbed energy occurs over many internal degrees of freedom, with the result that the life of the activated molecule is greatly increased and the chance for dissociation before ultimate collisional stabilization occurs is correspondingly decreased (29, 33, 48). An observed continuous absorption would in this case be "experimentally continuous", owing to the overlapping of a large number of closely spaced transitions. (c) In the majority of cases quantum yields have been based on rate of carbon monoxide evolution. In these cases any condensation reactions (5, 12) would reduce the apparent yield. (d) Deactivation by collision or fluorescence may be a contributing factor following absorption at longer wave lengths (e.g., acetone at 3130 Å.) (12).

Since theory b accounts for the low overall yield on the basis of a low primary yield, the question of chain length in the secondary reactions immediately becomes concerned. If the acetaldehyde photolysis at high temperatures proceeds entirely by reactions a1, a2, a3, a4, and a6, the rate of decomposition will be

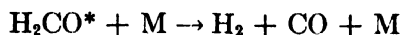
$$-\frac{d(\text{CH}_3\text{CHO})}{dt} = 2\phi I_{\text{abs.}} + \frac{k_3\phi^{1/2} I_{\text{abs.}}^{1/2}}{k_6^{1/2}} \text{CH}_3\text{CHO} \quad (2)$$

where ϕ is the primary quantum yield (reaction a1). The chain length, which will then be given by

$$\frac{k_3(\text{CH}_3\text{CHO})}{2k_6^{1/2}\phi^{1/2}I_{\text{abs.}}^{1/2}} \quad (3)$$

is inversely proportional to the square root of the primary yield. It follows that the absence of a chain in the high-temperature acetone photolysis cannot be inferred on the basis of the low quantum yield alone. The yield shows a high temperature coefficient from room temperature at least to 160°C., and the observed values may be due to a very inefficient primary process. The fact, however, that methyl radicals from other sources fail to initiate a chain in acetone is confirming evidence that no chain is concerned in the photolysis.

The observation of Norrish and Kirkbride (35) that formaldehyde vapor at 110°C. is decomposed by absorption of 3650 Å., which lies in the region of definite rotational structure, with a quantum yield almost as great as that for absorption in the continuum (0.7 versus 1.0) led these authors to the postulation that activated molecules may be dissociated by collision. Absence of atomic hydrogen (37) and the low energy of the absorbed quantum would both indicate a dissociation into finished molecules,



The increase in quantum yield with pressure for absorption in the banded region (3130 Å.) for both acetone (12, 19) and the butyraldehydes (26) has likewise been interpreted as indicating a dissociation induced by collisions. That such a phenomenon is not general is shown by the decrease in yield with increasing pressure for acetaldehyde at 3130 Å. Independence between yield and pressure at shorter wave lengths indicates that these effects are related to the production of activated molecules. The decrease in yield with increasing pressure for acetaldehyde may be interpreted as indicating collisional deactivation or the removal of activated molecules by polymerization. The high decomposition quantum yield for acetaldehyde at 3342 Å., which falls in the weak continuum between two bands, as compared with the low yield at 3130 Å., which falls directly on a band, is additional evidence in support of this view (25). In the case of acetone, data as to the nature of the process at 3130 Å. are conflicting. The $\text{C}_2\text{H}_6/\text{CO}$ ratio of unity indicates a dissociation into finished molecules (50), while the known production of methyl radicals at this wave length indicates a dissociation into radicals. The change in quantum yield with intensity (12, 25) is difficult to reconcile with collisional dissociation. The data are best explained on the basis of a coexistence of two primary processes due to the overlapping of two types of absorption,—discrete absorption, with the production of activated molecules which are either deactivated or dissociated into finished molecules by collision, and continuous absorption, with direct dissociation into radicals.

IV. POLYMERIZATION

Relatively little attention has been given to the photopolymerization of aldehydes and ketones, but the data available indicate that two distinct processes are concerned. With change in wave length from the region of structure and fluorescence to the region of continuous absorption, the quantum yield of apparent polymerization uniformly decreases for acetaldehyde (25), first decreases (3130 to 3020 Å.) then increases (3020 to 2537 Å.) for propionaldehyde (24) and *n*-butyraldehyde (26), and uniformly increases for isobutyraldehyde. At 3130 Å. the yield increases at least with the first power of the pressure, while at 2654 and 2537 Å. it may either increase (propionaldehyde) or be independent (acetaldehyde) of the pressure. The two processes thus suggested are (a) polymerization involving activated molecules and (b) polymerization induced by the radicals resulting from photodissociation by absorption in the continuum. Process a becomes successively less important and process b more important in the series from acetaldehyde to isobutyraldehyde.

A remarkable increase in the rate of polymerization with decreasing wave length has been observed by Blacet, Fielding, and Roof (5) for acrolein, the quantum yield at $P = 200$ mm. and $T = 30^\circ\text{C}$. changing from 0.3 at 3660 Å. (structure) to ~ 20 at 2654–2537 Å. (continuum). Blacet, Fielding, and Roof suggest a mechanism for the polymerization involving reaction of either CH_2CH , HCO , H , or more complex radicals with acrolein molecules, probably at the $\text{C}=\text{C}$ bond. The process concerned is probably to be compared with the polymerization of ethylene by methyl radicals (52).

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Addendum²

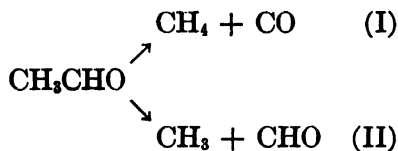
Since the completion of the preceding discussion the results of some unpublished work carried out by E. Gorin in Moscow, U.S.S.R., have been communicated privately to the Committee. The newer data may modify some of the preceding conclusions on the problem of mechanism in such photolyses.

Gorin has studied the photolysis of acetaldehyde, acetone, formaldehyde, and methyl ethyl ketone in the presence of iodine vapor. It has been shown that a few tenths of a millimeter pressure of iodine molecules is sufficient to react with all the free radicals formed in the primary process.

²Contributed by Hugh S. Taylor.

From analyses for the products RI and HI so produced, the number of radicals produced by the action of the light can be deduced.

With acetaldehyde-iodine systems Gorin finds methane and carbon monoxide in addition to methyl iodide. At a given wave length the ratio $\text{CH}_4:\text{CH}_3\text{I}$ is constant, independent of the temperature and of the pressure of iodine and aldehyde. There are, therefore, on this evidence, two primary processes



Gorin concludes that at 3130 Å. reaction II is 2.6 times as probable as I, but that at 2537 Å. reaction I is 2.9 times more probable. The quantum yield is unity for the formation of $\text{CH}_4 + \text{CH}_3\text{I}$ at both wave lengths. Gorin finds that HCO radicals do not react with iodine molecules below 100°C., but do react to give $\text{H}_2\text{CO} + \text{CO}$. The formaldehyde formed was equal to half the methyl iodide formed, and equal to the excess of carbon monoxide over methane formed by reaction I. Above 100°C. hydrogen iodide begins to be formed, suggesting that formyl radicals decompose at these temperatures. This gives a minimum value of 26 kg.-cal. for the activation energy of the reaction $\text{HCO} = \text{H} + \text{CO}$.

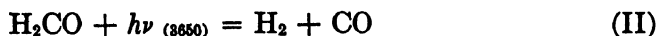
The evidence as to the influence of wave length on the alternative modes of decomposition is not in accord with other evidence on the relative amounts obtained from other studies (see page 751).

In the photolysis of acetone in presence of traces of molecular iodine no appreciable carbon monoxide formation was observed by Gorin below 60°C. Methyl iodide is formed, with a quantum yield of unity, at all wave lengths. Acetyl iodide in small amounts and diacetyl were qualitatively detected. This supports the conclusion that the primary process is represented entirely by process B of the preceding paper (page 750). The quantum yield of unity would appear to eliminate theories b and d (page 756) of the discussion by Leighton.

With formaldehyde and iodine, at all wave lengths below 3650 Å., only carbon monoxide and hydrogen iodide are formed in the ratio $2\text{HI}:\text{CO}$. The primary process should therefore be, exclusively,



At 3650 Å. hydrogen is also found, indicating the additional process



The relative probabilities are 2.5 for reaction I to 1 for reaction II. The ratio is not changed by replacing iodine with mercuric iodide as acceptor.

With methyl ethyl ketone and iodine, Gorin's results indicate that not more than a few per cent of the total primary process produces saturated hydrocarbon and carbon monoxide; the radical-producing processes are therefore overwhelmingly predominant. With acetaldehyde and iodine no polymerization was found by Gorin, indicating that it is the free radicals which are largely responsible for the polymerization observed during photolysis in the absence of iodine.

HYDROCARBON FREE RADICALS IN PHOTOPROCESSES¹

HUGH S. TAYLOR

Department of Chemistry, Princeton University, Princeton, New Jersey

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The communication by Leighton (10) on the mechanism of aldehyde and ketone photolysis has discussed in detail one group of photoreactions in which the primary process leads, at least in part, to the production of hydrocarbon free radicals. In the present communication will be reviewed a group of other photoprocesses in which the absorption of light also gives rise to the production of hydrocarbon free radicals, from the secondary reactions of which further data on the properties of such radicals and their reactivities with various atomic and molecular species can be deduced. From such studies are slowly accumulating a series of data, first qualitative and later quantitative, with the aid of which a more certain interpretation of secondary reaction paths can be deduced.

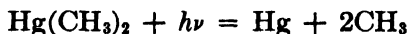
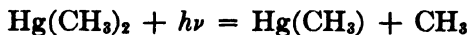
The photoprocesses leading, in the primary process of absorption, to the production of free radicals include the photolysis of alkyl iodides, the photodecomposition of metal alkyls, the mercury-photosensitized hydrogenations of unsaturated hydrocarbons, and the mercury-photosensitized decompositions of saturated hydrocarbons. As yet, the majority of the studies are confined to the simpler homologs of the several series of compounds, and the radicals for which the studies are least equivocal are the methyl and ethyl radicals.

THE PRIMARY PROCESSES

With the lighter alkyl iodides, which show regions of continuous absorption in the ultraviolet with well-developed band spectra of greater intensity than the continua, beginning near 2000 Å. and extending into the Schumann region, it is quite generally postulated (2, 7, 8, 22, 24) that the primary process leads to dissociation into a free radical and an iodine atom. Thus, with methyl iodide we assume the formation of $\text{CH}_3 + \text{I}$, and with ethyl iodide the formation of $\text{C}_2\text{H}_5 + \text{I}$. There are no data which conflict with this point of view. Differences in reaction product arising from such photolyses are, as we shall see, to be ascribed to secondary processes rather than to any other products of the primary absorption.

¹ Contribution No. 6 to the Third Report of the Committee on Photochemistry, National Research Council.

Of the metal alkyls the best investigated are those of lead and mercury. The spectrum of mercury dimethyl shows diffuse bands below 2150 Å., with an overlapping continuum which extends to about 2600 Å. (12). Terenin and Prileshajeva (20) interpreted this absorption as leading to primary dissociation into free radicals and detected such by their action in removing metallic mirrors. Linnett and Thompson (12), after first assuming that the major primary process was decomposition to mercury and ethane, finally decided that the facts could be best interpreted by the two possible free-radical decompositions



Leighton and Mortensen (11) confirmed the observations of Terenin (19) and of Duncan and Murray (5), that the absorption spectra of lead tetramethyl, tetraethyl, and tetraphenyl were all continuous, the long wave length limits of absorption by the vapors being 2800 Å. for the methyl and 3500 Å. for the ethyl compound. Lead tetraphenyl in solution in trimethylpentane gave an absorption limit around 2800 Å. These continuous spectra point to dissociation in the primary absorption act, with radicals or saturated molecules as possible products in addition to the metal atoms or metal radical complexes.

In the mercury-photosensitized hydrogenation of unsaturated hydrocarbons, when hydrogen is present in any marked amount, the primary process occurs between excited mercury and molecular hydrogen generating atomic hydrogen. The free radical arises as a secondary reaction between the atomic hydrogen and the unsaturated hydrocarbon. The simplest radical so produced is the ethyl radical from ethylene. All the recent evidence indicates that this is a process of good efficiency and that the presence of ethylene serves to reduce the stationary state concentration of atomic hydrogen to small values.

For the saturated hydrocarbons Bates (1) has shown that the quenching efficiency of methane for excited mercury is very small, but that with the higher homologs there is an increased quenching efficiency. The data of Morikawa, Benedict, and Taylor (13) suggest that quenching of methane even at room temperatures gives rise to $\text{CH}_3 + \text{H}$ either directly or by collision with metastable mercury atoms. Indirect evidence suggests that the dissociation process may require an activation energy of ~ 4.5 kg-cal. The efficiency increases with temperature.

A recent study of Steacie and Phillips (17) is concerned with the interaction, in a circulatory process, of excited mercury and ethane. They reached the conclusion that the products of the primary interaction between excited mercury and ethane are two methyl groups. The reaction



was ruled out because of the absence of molecular hydrogen in the reaction products. In the corresponding experiments with butane, Steacie and Phillips found abundant production of hydrogen. More recent experiments by these authors, not yet published, indicate that, in single-pass experiments in place of a circulatory process, the formation of hydrogen from ethane definitely occurs. This means that, with circulation, the hydrogen formed is converted into atomic hydrogen by photosensitization and is consumed in further reaction processes the nature of which will later be discussed.

THE QUANTUM YIELD

The alkyl iodides show remarkably low quantum yields, especially in the vapor state. Methyl iodide has a yield of 0.02 in terms of iodine atoms per absorbed quantum in the gaseous state (2), and 0.05 in hexane solution in the region of continuous absorption (25). With ethyl iodide, the yield is of the order of 0.01 at 2600 Å., increasing to 0.1 at 2026 Å. In the continuous region, liquid ethyl iodide and its solution in hexane show yields of about 0.6, whereas at 2026 Å. the yield has decreased to 0.24 (24).

The low yield in the continuum points to dissociation followed by recombination. This view is supported by recent experiments of West (23), in which photolysis in the presence of silver foil as a trap for iodine atoms increased decomposition fortyfold, with a marked change in the composition of reaction products (see later discussion). The solvent molecules, in the experiments in the continuum, also should repress dissociation, according to the Franck-Rabinowitch principle, so that the large influence of solvent on quantum yield needs special consideration. In the short wave banded region, West and Ginsburg assume the production of optically excited molecules and their interaction with normal iodide molecules.

With lead tetramethyl vapor Leighton and Mortensen (11) found quantum yields at 25°C. somewhat more in excess of unity (1.01-1.13) than could be attributed to experimental error. The authors therefore suspected the existence of short chains. Linnett and Thompson (12), with mercury dimethyl, found a quantum yield of unity at room temperature, but at higher temperatures the yield increased gradually to 2.2 at 190°C. Cunningham (4) found a more than threefold increase in mercury dimethyl vapor decomposed between 50° and 300°C. These results point to the better propagation of chains with increase in temperature.

In the mercury-photosensitized hydrogenation processes the quantitative extinction of mercury fluorescence by hydrogen is well known, and hence the quantum yield of the total process is dependent on the efficiency of the secondary processes. In the hydrogenation of ethylene the evidence points to a 100 per cent utilization of the primary products in these secondary processes. In the mercury-sensitized decomposition of ethane, Steacie

and Phillips found a quantum yield of approximately 0.2 in terms of ethane disappearing. This they ascribed, at least in part, to the inefficiency of the primary process of quenching by ethane. With butane a higher quantum yield, 0.55, was obtained.

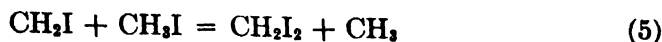
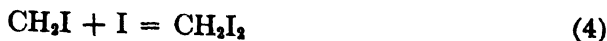
THE SECONDARY PROCESSES

The primary processes in the photolysis of methyl iodide, lead tetramethyl, mercury dimethyl and, according to Steacie and Phillips, in the photosensitized decomposition of ethane, all lead to the production of methyl radicals. There are, however, conspicuous differences in the products finally obtained.

In the case of methyl iodide, methane comprises 80 per cent of the product at room temperatures with from 4 to 12 per cent each of ethylene and ethane, for reactions in quartz vessels, packed or unpacked. With silver foil present, the methane yield fell to 28 per cent, while the ethylene and ethane yields rose to 18 and 54 per cent, respectively, ethane becoming in this case the major product. As much as 36 per cent of the methyl iodide disappearing is recoverable as CH_2I_2 . Ethane predominates almost to the exclusion of other products in the photolyses of lead tetramethyl and mercury dimethyl. Linnett and Thompson found from 7 to 10 per cent of methane and 0 to 5 per cent of ethylene with about 90 per cent of ethane. They do not record any variation in product with temperature change. Cunningham found ethane with negligible amounts of methane and ethylene from room temperatures to 160°C . Beyond this temperature the methane yield increased to about 20 per cent of the hydrocarbon product at 300°C . In the photolysis of acetone similar results obtain. At 70° and 160°C . the hydrocarbon is more than 90 per cent ethane; at 300°C . equal volumes of ethane and methane are formed. In the Steacie-Phillips experiments with excited mercury any methyl radicals are formed in the presence of excess ethane. Hence no conclusion as to the amount of ethane which is regenerated can be given. Of the other hydrocarbons, nearly 60 per cent is methane, 23 per cent propane, and nearly 20 per cent butane. The butane undoubtedly arises from recombination of two ethyl radicals, since this gas is the predominant product in the mercury-photosensitized hydrogenation of ethylene (9).

The low quantum yield and the abnormal products in the methyl iodide decomposition are accounted for by West with the following sequence of reactions:

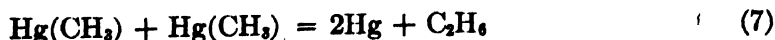
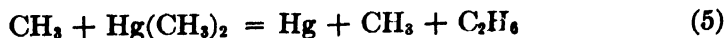
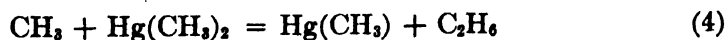
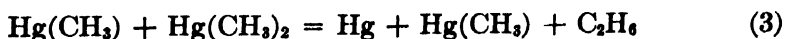
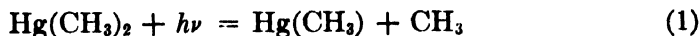




It is evident that the recombination reaction (reaction 2) must be exceedingly efficient to account for the low quantum yield. All other processes are minor in comparison with processes 3, 4, and 5, the most important to account for the products found. West estimates that an activation energy of 10 kg-cal. for reaction 3 in competition with reaction 2 would account for the observed quantum yield. In agreement with this estimate are some measurements of Ginsburg (6), indicating an increase of quantum yield with temperature in the case of ethyl iodide photodecomposition.

Reaction 2 must also be rapid in comparison with reaction 9 which forms ethane. A steric factor of the order of 10^{-4} or 10^{-5} has been ascribed to the association of two methyls by Bawn (3). When, however, the iodine atoms are trapped by silver foil, reaction 9 appears to compete favorably with the methane-producing reaction (reaction 4).

A sequence of reactions to account for the photolyses of mercury and lead methyls is suggested by the following scheme of Thompson and Linnett:



In these cases the recombination process



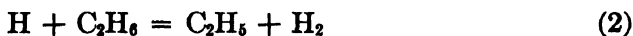
must be of lower probability than in the case of the iodide in view of the quantum yield of ~ 1 . That it occurs to some extent is known from

work of Paneth and others on the removal of mirrors by methyl radicals. Taking this into account, the quantum yield of unity at room temperatures signifies that some chain propagation is already occurring at these temperatures. Reactions 3, 4, and 5 are chain-propagating stages. They must possess an activation energy, otherwise a quantum yield of $\sim 10^6$ might be expected. Thompson and Linnett calculate that an activation energy of ~ 11 kg-cal. for the chain-propagating reactions is in accord with the quantum yield of unity at ordinary temperatures and of 2.2 at 200°C . The presence of only traces of methane in the room temperature product indicates that, owing to the weakness of the Hg—C bond, this is broken in preference to the C—H bond in the mercury alkyls struck by methyl radicals. Since about 20 per cent of the hydrocarbon is found as methane at 300°C . this suggests that the breaking of the C—H bond must have an activation energy some 2 kg-cal. higher than that required for the breaking of the Hg—C bond.

Molecular hydrogen does not readily react with methyl radicals until temperatures of 160°C . and upwards are reached (13, 18, 21). The activation energy of the process has a value of 9 ± 2 kg-cal. The interaction of atomic hydrogen with methane is to be assigned a somewhat higher value (16, 21) of 13 ± 2 kg-cal. and is insignificant below 250°C . Interaction with ethane is much more easily obtained, some interaction occurring at room temperatures. Trenner, Morikawa, and Taylor (21) ascribed this to a reaction



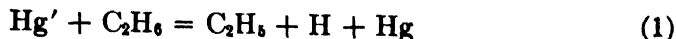
The argument developed by them to exclude a reaction sequence



is not entirely compelling. It is well known that F. O. Rice's free-radical mechanism (15) is incompatible with the ready occurrence of the first of these interactions.

The absence of methane, in the photosensitized hydrogenation of ethylene, until all the ethylene is hydrogenated, even though ethyl radicals and ethane are present, may be due to the low stationary state concentration of atomic hydrogen in presence of ethylene. Careful test by Jungers and Taylor (9) failed to reveal any significant amounts of methane with reaction in vessels kept carefully free from hydrocarbon deposits of higher molecular weight. Under these conditions also, the predominant product is butane, obviously by combination of ethyl radicals. The low relative production of ethane or propane is additional evidence of low hydrogen atom and methyl radical concentrations in such systems.

In the photosensitized decomposition of ethane, Steacie and Phillips now favor the C—H bond split by a reaction



They favor the reaction



to account for their observed methane formation. For the reasons just discussed one is forced also to consider the possibility



as the source of methyl radicals, subsequently converted to methane and propane by the recombination processes,



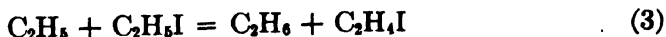
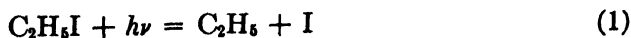
The recombination of ethyl radicals would produce the observed butane as in the photosensitized hydrogenation of ethylene. Unless one accepts reaction 3 as the mode of production of methyl radicals one is forced to conclude, as Steacie has called to the attention of the writer, that reaction 2 must be at least four times faster than

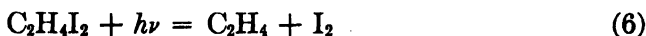
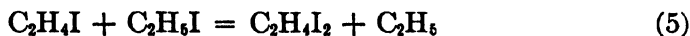


Otherwise hydrogen would not be *consumed* in the photosensitized interaction of hydrogen-ethane mixtures. The difficulties of the F. O. Rice chain mechanisms (15) would once more be acute. Rice and Teller, from a theoretical analysis, also strongly favor the mechanism. It is quite evident that there is need for further study in this field.

Contrasting with the relatively large butane formation in the photosensitization experiments are the products from the photolysis of ethyl iodide vapor. Here, as West has shown, the products are predominantly ethane and ethylene, with no butane and with minor amounts of hydrogen and methane. As in the case of the methyl radicals from methyl iodide it is the secondary processes which must account for the non-formation of butane.

The sequence of reactions suggested by West is:





Of these reactions 3, 4, 4a, and 6 are the essential secondary reactions which account for the decomposition. The reactions must occur more readily than the methyl reactions, since even in presence of silver foil no butane was observed.

The increased yield in the photolyses of the alkyl iodides in the liquid or dissolved state over that in the gaseous state is ascribed by West, at any rate in part, to the action of the solvent molecules in providing third bodies for the yield-increasing radical associations. This influence must be exercised preferentially on the atom reaction $\text{I} + \text{I}$ which certainly requires a third body, whereas the radical recombinations and $\text{CH}_3 + \text{I}$ and $\text{C}_2\text{H}_5 + \text{I}$ probably occur, at least in part, as association reactions. The interactions of the radical-iodine atom systems must be more efficient than the radical recombinations as the quantum yield is so low. West has shown that an inert gas such as carbon dioxide at a pressure of 10 to 40 atm. exercises an influence similar to solvent molecules in raising the quantum yield, a pressure of 40 atm. exercising an effect approximately 13.5 per cent of that obtaining in hexane solution.

In addition to the influence of solvent as third body in recombination processes there is a possible influence due to secondary reaction with the radicals. Recent work of Norrish and Bamford (14) has shown that radicals from the photolysis of ketones may remove hydrogen atoms from saturated hydrocarbon solvent molecules, becoming saturated thereby and producing, ultimately, unsaturation in the solvent. This possible effect has not yet been studied in alkyl iodide systems.

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Addendum

The previous discussion might also have included the recent work from the New York University laboratories on the photolysis of azomethane as the source of free methyl radicals (Burton, Davis, and H. A. Taylor: *J. Am. Chem. Soc.* **59**, 1038, 1989 (1937); Davis, Jahn, and Burton: *J. Am. Chem. Soc.* **60**, 10 (1938)). The quantum yield of this photolysis has been carefully studied by Forbes, Heidt, and Sickman (*J. Am. Chem. Soc.* **57**, 1935 (1935)) with six monochromatic radiations at four pressures from 180 to 665 mm. The quantum yield approached unity as its upper limit for initial decomposition and a temperature increase from 20° to 226°C. had no effect on the quantum yield. The latter fell with increasing pressure. These results led the authors to the conclusion that the photolysis was not a chain reaction.

Burton, Davis, and Taylor have made a careful analytical study of products of the photolysis in the temperature range -22.5° to 223°C. In every case there is an excess of nitrogen formed, about 55 per cent at room temperatures rising to a maximum of 69 per cent at about 220°C. Methane in the hydrocarbon product is about 7 per cent by volume at room temperature and increases to 70 per cent by volume at 220°C. Ethane, which represents more than 90 per cent at room temperature, decreases to 15 per cent at 220°C. In the higher temperature range propane and possibly butane, in small amounts, are increasingly produced. Hydrogen and unsaturated hydrocarbons are not formed in measurable amounts.

There is no doubt that the majority of these results are consistent with a primary act producing free methyl radicals with minor, if any, intramolecular rearrangement to form stable molecules. The change in the character of the hydrocarbon products with temperature is consistent with the data on the reactions already discussed. In the case of the azomethane photolysis, however, there is quite evidently a more marked interaction between the free radicals and the azomethane, presumably to yield hydra-

zines, than is the case in several of the other substances described. The overall reaction becomes correspondingly more complex, the authors being of the opinion that the ethane formed results, not from the recombination of the methyl radicals, but from decomposition of the more complex radicals and molecules. In view of the preceding discussion this conclusion should be accepted with great reserve.

THE EVALUATION OF SPECIFIC REACTION RATES IN CHAIN REACTIONS¹

G. K. ROLLEFSON

Department of Chemistry, University of California, Berkeley, California

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One task involving photochemical chain reactions which has been undertaken by many investigators is that of evaluating the specific reaction rates (or rate constants) for the various steps which occur. The problems which arise with each reaction studied are so similar that the discussion will be simplified if we consider the three main types of processes: (1) chain starting, (2) chain terminating, (3) chain continuing.

I. CHAIN-STARTING REACTIONS

A consideration of the mechanisms which have appeared in the literature leads to the conclusion that chains are started by some kind of an odd molecule, either an atom or a free radical, and are propagated by the alternate formation and disappearance of such molecules. Therefore, in this discussion, we are concerned with the rate of formation of odd molecules as a result of light absorption. In the simple cases, such as the absorption of light by diatomic molecules in the gaseous state in a continuous absorption band, it has been quite well established that dissociation occurs for every light quantum absorbed. The same may be said for the truly continuous absorption by more complex molecules, although, in such cases, it may be difficult to decide whether the spectrum is really continuous or only appears to be so because of inadequate resolution. Very often, however, we must consider a competition between the dissociation process and other processes such as fluorescence, deactivation by collision, or some reaction of the photoactivated molecule, either by itself or with other molecules, which does not involve the formation of odd molecules. For example, the photodecomposition of acetaldehyde at high temperatures is a chain reaction probably involving methyl radicals (15). From the work on this reaction at lower temperatures we know that, in the first stage, we have competition between fluorescence, a polymerization reaction, and probably a direct decomposition into methane and carbon monoxide as well as the dissociation to give methyl radicals (16, 27). It is appar-

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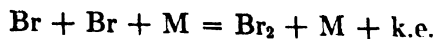
ent, therefore, that in this case it would be definitely inaccurate to set the number of chains started equal to the number of quanta of light absorbed. This uncertainty is involved in every reaction in which the radicals are produced by a predissociation process. A similar uncertainty is introduced if we have two overlapping absorption bands corresponding to transitions to two different excited states. Even with such a simple molecule as chlorine, Aickin and Bayliss (1) have shown that the continuous absorption is complex and there is a continuum underlying the sharp line bands. In this case Bayliss (3) has shown that the observed facts concerning the combination of hydrogen and chlorine caused by light absorbed in the banded region of the spectrum can be accounted for by assuming that only the continuous absorption starts the reaction chains.

Another source of uncertainty as to the efficiency of the dissociation process was suggested by Franck and Rabinowitch (11). They expressed the view that the quantum yield of a primary dissociation process in solution must be very low, as the surrounding molecules will prevent the separation of the parts. Rollefson and Libby (28) pointed out that such an effect should be observed if the speed of the separating parts is small, but most experiments have been performed with such energies that the parts would be separating with relatively large kinetic energies and thus be able to break through the surrounding cordon of solvent molecules, making the dissociation practically as efficient as in the gas phase. Dickinson (8) has discussed a number of reactions in solution and shown that they could be most readily explained by assuming that the first step was a dissociation of the light-absorbing molecule. Rabinowitch (22) has objected to such arguments on the grounds that the rate considerations used by Dickinson and others depend on the steady state concentrations of radicals or atoms rather than on their rates of formation, and these steady state values could be unchanged if the rates of dissociation and recombination were affected equally by the solvent. Rollefson and Libby pointed out that such a symmetrical modification was unlikely. Furthermore, it must be said that it is difficult to conceive of chains which are unaffected by dilution having a length such that the quantum yield of the overall reaction would be 2; yet such an assumption is necessary for ClO_2 in carbon tetrachloride solution if we do not assume a high efficiency for the primary step.

II. CHAIN-TERMINATING REACTIONS

The best known of the chain-terminating reactions are those involving the recombination of atoms. Many studies with atomic hydrogen have shown that the recombination occurs at every collision during which a third body is present to remove some of the energy (2, 10, 32). Similarly, a comparison of the thermal and photochemical rates of formation of hydrogen bromide has led to the conclusion that bromine atoms recombine by a

triple collision mechanism (5, 14). Ritchie (23) and Hilferding and Steiner (13) have studied the relative efficiencies of different molecules as the third body. Some idea of the range encountered is given by rate constants for the reaction



taken from the paper by Hilferding and Steiner (see table 1). The variation is very similar to that found for the quenching of fluorescence by these gases. On the basis of these observations it seems reasonable to assume that any atom recombination process occurs at approximately every triple collision if the reaction is homogeneous.

The heterogeneous recombination of atoms depends quite markedly on the nature of the surface involved. It was found in the very first experiments with hydrogen atoms that dry glass or quartz surfaces are very much more effective in causing the recombination than ones which had not been dried (33). Metallic surfaces were also found to be very effective in causing recombination. Experiments with the hydrogen-bromine

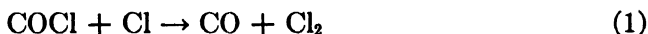
TABLE 1
Rate constants for Br + Br + M

M.....	H ₂	He	A	N ₂	Br ₂	HBr	HCl	CO
<i>k</i> × 10 ⁻¹⁵	1.25	0.47	0.11	0.82	2.6	2.1	4.7	6.3

reaction at such pressures that the bromine atoms recombine on the wall show that the rate depends on the previous treatment of the walls (13). Another example is found in the hydrogen-chlorine reaction in which Bodenstein and Winter (6) calculated that only one collision in six thousand on a silver chloride surface resulted in removal of the chlorine atom. A comparison of their quantum yields with values obtained in the presence of glass surfaces indicates that glass is about ten times as effective. The failure of the atoms to react at every collision with the surface does not seem to be due to the requirement of any heat of activation, but rather to a low value of the accommodation coefficient. This idea is supported by a comparison of the photochemical temperature coefficients for the hydrogen-chlorine reaction as obtained by Hertel (12) and by Potts and Rollefson (21) with the value obtained by Rodebush and Klingelhoefer (24) for the reaction of chlorine atoms with hydrogen molecules, which shows that the latter reaction is capable of accounting for the entire temperature coefficient of the former. The principal difficulties in the way of securing exact values for the rate constant of such a chain-terminating reaction are the determination of the accommodation coefficient and the rate of approach to the wall. The latter rate is complicated by the fact that, usually, the heat of reaction sets up convection currents which make it

virtually impossible to decide on an average path length. On the whole, the error in the estimation of the rate of a chain-terminating process involving atoms is probably not greater than a factor of one hundred, whether it is a homogeneous or a heterogeneous reaction.

If the chain-terminating reaction involves more complex groups, more varieties of reaction are introduced. The surface reactions and the triple collision mechanism for association reactions are possible here as well as with atoms. However, it cannot be said with certainty that the association reactions do not involve heats of activation. Furthermore, it is possible for two radicals to combine to form a single molecule by a process which is the reverse of predissociation without having a third body present. In such a case, the quasi-molecule formed would have a sufficiently long life to lose some of its energy in a collision and become a stable molecule. Finally we have the possibility of two radicals reacting to form normal molecules. Some examples of these types of reaction which have been assumed are

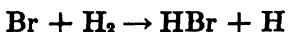


* As the concentrations of these radicals are always very low, trimolecular processes involving them must be considered improbable.

The evidence for these reactions is not very conclusive, as the experiments have been such that other possibilities have been present. In support of reaction 2 we may cite the formation of ethane in the photolyses of lead tetramethyl (17), acetone (18), or methyl ethyl ketone (19). Reaction 3 has been assumed frequently, but probably the best evidence for it is the formation of ethane and ethylene in the photolysis of ethyl iodide (9). The magnitudes of the activation energies for these reactions are at present unknown. They are probably not large, but even a small activation energy would introduce a rather large uncertainty into the specific reaction rate. Until further data are available, we must conclude that the constants for reactions between two radicals are not sufficiently well known to be used in calculating rates of photochemical chain reactions.

III. CHAIN-CONTINUING REACTIONS

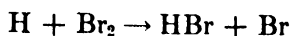
The direct measurement of the rate constants for reactions of the type involved in the propagation of chains has been limited to a very few cases involving atoms. Most of these reactions involve hydrogen or one of the halogen atoms. The specific rate of the reaction



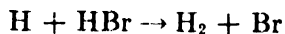
can be obtained from the thermal rate of formation of hydrogen bromide if we assume that bromine atoms and molecules are in equilibrium in the reaction mixture. On the basis of data obtained from the experimental study of both the thermal and photochemical formation of hydrogen bromide, Bodenstein and Lütke Meyer (5) give for the rate constant

$$\log k = - \frac{3859}{T} + 13.862$$

which corresponds to an activation energy of 17,640 cal. The reaction is endothermic to the extent of 14,500 cal., so the activation energy is only slightly greater than the energy required to offset the endothermicity of the reaction. The study of the rate of formation of hydrogen bromide also tells us that the ratio of the rate constants for the reactions

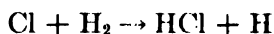


and



is 8.6 over a very wide temperature range. This fact suggests that the heats of activation for these reactions are zero, the only difference being in the so-called "steric factor".

The rate of the reaction



was measured directly by Rodebush and Klingelhoefer (24), who used a known concentration of chlorine atoms produced by an electric discharge in chlorine gas. They found that the rate was given essentially by the number of collisions multiplied by $e^{-6000/RT}$ with the uncertainty in the numerator of the exponent being approximately 1000 cal. A similar value was obtained from the measurements by Hertel (12) and by Potts and Rollefson (21) of the temperature coefficient of the photochemical reaction of oxygen-free mixtures of hydrogen and chlorine, if it was assumed that the chain-terminating step involved no heat of activation.

A number of reactions of hydrogen atoms have been studied by preparing a measurable concentration of the atoms by means of an electrical discharge and passing these atoms into some other gas. The most important reaction studied by this method is the transformation of para-hydrogen into ortho-hydrogen. The fraction of the collisions between hydrogen atoms and hydrogen molecules which result in reaction is 2×10^{-6} and the heat of activation is approximately 7000 cal. Other reactions which have been tried include those with oxygen, water, the halogens, the hydrogen halides, some hydrocarbons, hydrogen sulfide, and methyl halides. Under these conditions most of these reactions proceed too fast to obtain accurate measurements, so the only conclusion which can be drawn is that the hydrogen atoms are destroyed in less than one hundredth of a second,

which means that at least one collision in 10^4 is effective. The activation energy is therefore either zero or very small.

Other methods which have been used to obtain estimates of the rates of the steps in a chain process are (1) studies of the overall rate with appropriate assumptions concerning the chain-starting and chain-terminating reactions, and (2) studies of systems in which two reactions compete for the same reactive intermediate. The validity of both of these methods depends on the assumption that the mechanism used in the calculation is correct. It is essential therefore that any other mechanisms be excluded on the basis of the experimental evidence before rate constants obtained by these methods may be considered valid. We may illustrate the first method by referring to the formation of hydrogen chloride from the elements. The mechanism which seems to explain the behavior of oxygen-free mixtures of hydrogen and chlorine is expressed by the following equations:



This leads to the rate expression

$$\frac{d(\text{HCl})}{dt} = \frac{k_1 k_2}{k_4} I_{\text{abs.}}(\text{H}_2)$$

If the light absorbed corresponds to the continuum in the chlorine spectrum, there is plenty of evidence to support the assumption that $k_1 = 2$. The constant k_4 is subject to much greater uncertainty. Usually, it is assumed that every collision of an atom with a surface is effective in causing recombination, but recently Bodenstein and Winter (6) have presented data which indicate that only one collision in six thousand of chlorine atoms with a silver chloride surface leads to the formation of molecules. This effect does not seem to be due to a heat of activation but rather is an accommodation coefficient analogous to the steric factor for bimolecular reactions. Collisions with glass or quartz surfaces are much more effective, but it is probable that the erratic rates of formation of hydrogen chloride that have been reported are at least partially due to the variation of this k_4 in different experiments. If we assume that reaction 4 has no heat of activation, then the entire heat of activation for the overall reaction is due to reaction 2. The value of k_2 may be calculated approximately by multiplying the collision number by $e^{-Q/T}$, where Q is the heat of activation. The efficiency factor for collisions between molecules possessing the necessary energy cannot be determined any more exactly than we

know k_4 . Usually in systems of this type the uncertainty in the heat of activation is sufficient to mask any uncertainty in the collision number or efficiency factor.

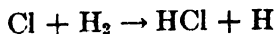
This type of calculation may be applied, with the same degree of approximation, to any other chain reaction involving atoms in the initial and final steps and having the rate determined by one step in the chain process. If radicals are involved in the initial or final steps, both of the uncertainties become much greater particularly on account of the activation energy of the chain-terminating step. Thus a reaction such as



which Schumacher and Wolf (31) assumed to be the chain-terminating step in the chlorination of chloroform probably requires some heat of activation, but the magnitude of this heat is not even approximately known. The same statement can be made about the other processes which we have discussed in the section on chain-terminating processes.

A further complication arises frequently owing to the complexity of the assumed mechanism. Thus, instead of having the overall rate constant expressed in terms of the constants for initial and final steps and one step of the chain (k_2 in the case of the formation of hydrogen chloride) we find that the constants of two or more steps of the chain appear in the rate equation. Such constants are indeterminate from rate measurements alone, and up to the present time no one has determined the constants for any system of this type from experimental data.²

The second method for evaluating the constants of steps in a chain, the use of competitive reactions, has not been used very extensively as yet. We have already cited the competition between hydrogen bromide and bromine for hydrogen atoms in the formation of hydrogen bromide. Other examples which have been studied quantitatively include the competition of carbon monoxide and hydrogen for chlorine atoms (4, 26), of oxygen and chlorine for COCl (25, 29), and of ozone and oxygen for oxygen atoms (30). The experiments determine only the ratio of the two rate constants but if one rate constant, as, for example, that for the reaction between atomic chlorine and hydrogen, is known from other studies, then the other can be calculated. We have already seen that the rate constant for the reaction



² Bodenstein and his students claim to have made such determinations for the formation of phosgene, but the details of their calculations have not been published. It may be remarked here that in their published work they have neither proven their mechanism to the exclusion of others nor listed enough independent equations based on experimental data to determine all of the constants involved in their rate equations. See, however, contribution No. 9 to this Report

is pretty well known, therefore we may use this reaction as a means of measuring chlorine-atom concentrations in reaction mixtures and thus the specific rates of other reactions. Naturally this method is limited to those systems in which the chlorine atoms react at a rate comparable with that with hydrogen. Thus, the observation that in mixtures of ethylene, hydrogen, and chlorine the halogen adds to the ethylene with no appreciable formation of hydrogen chloride tells us that the first step in the addition reaction is very fast but does not permit an exact calculation of its specific rate.

Many reactions of hydrogen atoms have been studied by determining the concentration of the atoms by the rate of the conversion of para-hydrogen to ortho-hydrogen. This is essentially the method of competing rates, except that the atoms are not destroyed by the test reaction. The rate constant for this conversion has been given as $2 \times 10^9 T e^{-7000/RT}$, which indicates the order of magnitude of the rates which may be studied by this method. One point which has been overlooked in some investigations is that if the hydrogen atoms react very rapidly with other substances in the reaction mixture the concentration of the atoms may not be great enough to cause appreciable conversion of para-hydrogen to ortho-hydrogen. This method has been applied by Cremer, Curry, and Polanyi (7) to the study of reactions of atomic hydrogen with alkyl halides. Their results were only semiquantitative and their experimental method limited them to reactions for which the activation energy was in the range $2800 < Q < 7200$ cal. Farkas and Sachsse (10) studied $H + O_2 \rightarrow HO_2$ and $H + CO \rightarrow HCO$. They concluded that the former occurred once in seven hundred fifty triple collisions and the latter once in ten triple collisions. Patat (20) has also used this method to determine the concentrations of hydrogen atoms present during the decompositions of a number of organic compounds. On account of the complexity of such systems only qualitative results concerning rate constants were obtained.

In conclusion, it must be stressed that the great need at present is the determination, by methods free from assumptions, of a few rate constants for reactions of the type we have discussed. No matter how reasonable assumptions may seem, any rate constants based on them are little better than guesses. This is especially true in complex systems as, under such conditions, usually several mechanisms are capable of describing the facts, and hence there is no certainty that we are dealing with the right set of reactions. The constants which have been calculated for such systems in the literature must be looked upon as reasonable interpretations rather than as established facts.

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THE SECONDARY PROCESSES IN THE PHOTODECOMPOSITION OF AMMONIA AND HYDRAZINE¹

HUGH S. TAYLOR

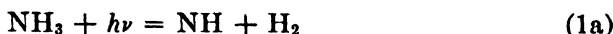
Department of Chemistry, Princeton University, Princeton, New Jersey

Received May 25, 1938

Since the diffuse bands of the ammonia spectrum were interpreted by Bonhoeffer and Farkas (1) as due to a dissociation of the molecule, the direction of further research on the photodissociation process has been towards an elucidation of the secondary processes in such a manner that the low quantum yield (~ 0.2) might be satisfactorily explained. For the primary process, it has been generally assumed that



though the reaction,



cannot be excluded on energetic grounds. It would, however, suggest an influence of molecular hydrogen which is not found experimentally in the photoreaction, although there is an effect in the reaction initiated by α -particles and ions, in which case, at higher pressures, NH^+ is certainly formed by secondary processes. The first reaction accounts for the presence of atomic hydrogen, made certain by the measurements of Geib and Harteck (6) and of Farkas and Harteck (4) on para-hydrogen conversion in ammonia undergoing decomposition.

Gedye and Rideal (5), using a streaming system, obtained yields of hydrazine from the photodecomposition of ammonia of as high as 57 per cent of the stoichiometric yield by the equation

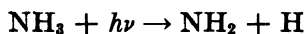


The hydrazine yield decreased rapidly as the temperature of the system was increased. Koenig and Brings (7), and more recently Weige and Beckman (16), have obtained positive confirmation of the formation of hydrazine by photolysis of ammonia in a static system. The amounts obtained, however, were very small.

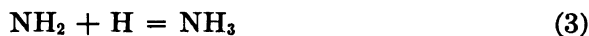
Indirect evidence of the production of amine radicals may be obtained from the photodecomposition of solutions of alkali metals in liquid am-

¹ Contribution No. 8 to the Third Report of the Committee on Photochemistry, National Research Council.

monia (13). Liquid ammonia does not photodecompose when pure, but does decompose on the addition of alkali metals. The sole products are hydrogen and amide ion, NH_2^- , in equivalent amounts, and the quantum yield is well under unity. Alkali metals virtually completely dissociate in liquid ammonia into positive metal ions and free electrons which become strongly solvated with the ammonia. It would appear, therefore, that in pure liquid ammonia deactivation or primary recombination effectively retards the decomposition, while in the presence of solvated electrons the NH_2 radicals are stabilized by the formation of amide ion, thus permitting the decomposition to proceed. The mechanism, according to this hypothesis, would be

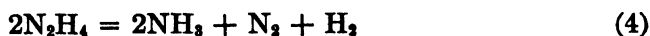


The majority of workers have accounted for the low quantum yield in ammonia decomposition by a recombination process,



though Farkas and Harteck (4) pointed out certain difficulties in accepting this, due to the low stationary state concentration of atomic hydrogen, especially if reaction 3 requires a third body. That ammonia is regenerated during the secondary processes was made definite by Taylor and Jungers (15), who showed the formation of deuterioammonias in mixtures of decomposing NH_3 and deuterium atoms produced from deuterium molecules by excited mercury. No exchange occurred unless the ammonia was undergoing photodecomposition. By investigating the photochemical decomposition in the region of very small decompositions Welge and Beckmann (16) found that the quantum yield measured by hydrogen produced approached unity; hence they concluded that the recombination reaction (reaction 3) does not play an important rôle. The products in such circumstances would be substantially hydrogen and hydrazine. They further assumed the secondary processes to be substantially heterogeneous, with a little of the hydrazine reacting with the atomic hydrogen to give ammonia, as shown by Dixon (2). With larger amounts of products this effect would be exaggerated and the non-condensable products would approach the stoichiometric ratio due to hydrazine decomposition.

In experiments of Elgin and Taylor (3) it was shown that the total process in both the photochemical and photosensitized decomposition of hydrazine can be with fair accuracy expressed by the stoichiometric equation

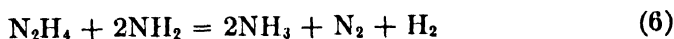


With hydrazine in the presence of ammonia, even when only a small fraction of the light was absorbed by the hydrazine, it was shown, by Ogg, Leighton, and Bergstrom (14), that hydrazine was the compound which disappeared, with a quantum yield of 1.28 on total quanta absorbed. Such facts provide considerable support for their conclusion, recently restated by Mund and van Tiggelen (12), that the process which regenerates ammonia and causes the low quantum yield is not reaction 3 but the reaction

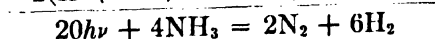
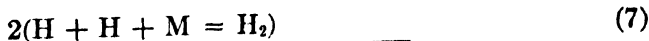
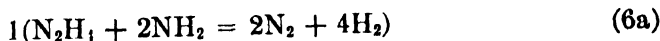
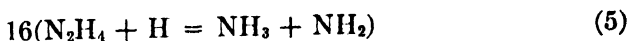
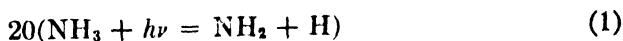


a reaction which would also explain the work of Taylor and Jungers with deuterium atoms.

The nitrogen which is formed ultimately in the photodecomposition of ammonia must arise, therefore, from further decomposition of the hydrazine or NH_2 radicals or both. The assumption of Ogg, Leighton, and Bergstrom that this occurs by the reaction



has been modified by Mund and van Tiggelen in a sequence of secondary processes which more satisfactorily than any alternatives, it would appear, accounts for the kinetics of the reaction and its quantum yield. The sequence is:

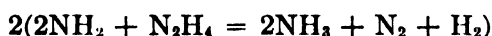
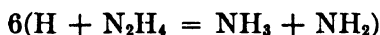
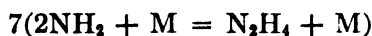
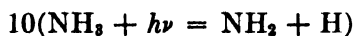


This sequence is based on a quantum yield of 0.2 at 1 atm. pressure, and the numerical coefficients by which the equations are multiplied must evidently be proportional to the velocities of the corresponding reactions. It leads to the following expression of Mund and van Tiggelen for the quantum yield

$$\Phi = \frac{1}{0.875 + \sqrt{0.0156 + K\sqrt{P/v}}}$$

where v ($\alpha I_{\text{abs.}}$) is the velocity of reaction expressed as the number of molecules of ammonia decomposed to nitrogen and hydrogen per cubic centimeter per second, P is the total pressure, and Φ the quantum yield equal to Q/v , where Q is the number of ammonia molecules per cubic centimeter per second primarily decomposed.

This equation reproduces the tendency of Φ to vary with the pressure. With $\Phi = 0.2$ at 1 atm. one calculates a value of $\Phi = 0.314$ at 0.1 atm. and 0.126 at 8.5 atm. The former is in agreement with the data of Wiig (18) and the latter with the measurements of Ogg, Leighton, and Bergstrom. At low pressures the influence of the walls begins to predominate and will assist especially reactions 2 and 7. Its effect on the quantum yield will be equivalent to that of high pressures in the gas phase, i.e., will lower the quantum yield as Wiig observed. The influence of the intensity or the velocity of decomposition, v , on the quantum yield is of the same order of magnitude as the equation suggests, as elucidated in a recent research by Mund, Brenard, and Kaertkemeyer (11), and as suggested by the work of Ogg, Leighton, and Bergstrom, by Wiig and Kistiakowsky (20), and by more recent measurements of Wiig (19). The Mund-van Tiggelen numerical values for the relative rates of the several reactions do not constitute a unique solution, as is evident from an analysis by Leighton (8). For the ratios 20:17:16:1:2 of the above sequence, Leighton substitutes the sequence



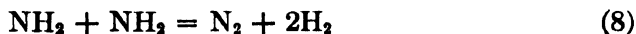
It will be noted that in this sequence the nitrogen-producing mechanism simultaneously regenerates ammonia, whereas the Mund-van Tiggelen reaction does not. Both yield similar expressions for the relation between quantum yield, pressure, and intensity. Leighton believes his reaction producing nitrogen to be superior, because it accounts for the 1:1 $\text{N}_2:\text{H}_2$ ratio observed in the ammonia-sensitized decomposition of hydrazine (see later).

It has been known since Warburg's original researches on this reaction that neither molecular nitrogen nor hydrogen influenced the quantum yield. The above mechanism is in accord with such inertness except in so far as it might influence the total pressure, P ; this influence is small, as seen. On the other hand, atomic hydrogen was shown by Melville (9) to inhibit strongly the photodecomposition of ammonia and the same is true of the photosensitized decomposition (10). This effect, which Melville attributed to the recombination reaction (reaction 3), is rather to be ascribed to the ammonia regenerative reaction with hydrazine (reaction 5), the velocity of which, as is to be seen from the magnitude of the molecular coefficient, 16, is very high. Analysis shows that in addition to the effect

of atomic hydrogen concentration there is also an effect due to the diminution in v , the total decomposition. The cumulative effect of these two factors is evident in the data both of Mitchell and Dickinson and of Melville.

Farkas and Harteck found a sharp maximum in the atomic hydrogen concentration from the photodecomposition of ammonia in the presence of hydrogen when the ammonia was only 10 mm. in a total pressure of 30 to 70 cm. This led these authors to the assumption of NH_4 radicals in equilibrium with $\text{NH}_3 + \text{H}$. The maximum should bear some relation to the maximum observed in the quantum yield but this latter, though similar in form, is displaced to higher ammonia pressures. This discrepancy is not yet elucidated.

The objection that might be raised to the Mund-van Tiggelen development, namely, that nitrogen only results from the termolecular process (from $2\text{NH}_2 + \text{N}_2\text{H}_4$, reaction 6) and not from such a process as suggested, among others, by Wiig,

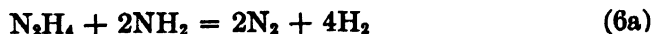


is discussed in the original communication of Mund and van Tiggelen and more recently by them in a comment on the newer work of Wiig. They point out that reaction 8 always leads to kinetic expressions from which the observed increase of quantum yield with velocity of decomposition cannot be deduced, and, further, it fails to account for the small variation of yield between 1 and 8.5 atm. found by Ogg, Leighton, and Bergstrom. One might expect that other molecules than N_2H_4 could act each with a particular efficiency in the recombination-decomposition process (reaction 6) of the Mund-van Tiggelen scheme. To introduce such possibilities into the kinetic scheme would further complicate the equation derived, and the experimental data at present are not accurate enough to justify, such further refinements.

In the ammonia-sensitized hydrazine decomposition experiments of Ogg, Leighton, and Bergstrom, the two initial stages are quite clear, namely, reactions 1 and 5 of the ammonia scheme above.



The Mund-van Tiggelen mechanism would then give



which would mean a quantum yield of 2 at a maximum diminished by the recombination process,



The product gas should be 33 per cent nitrogen and 66 per cent hydrogen. The Ogg, Leighton, and Bergstrom mechanism would give

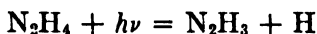


again a maximum quantum yield of 2 on the hydrazine disappearing but a 1:1 ratio of nitrogen and hydrogen. This ratio was actually found by these authors and also by Elgin and Taylor. Wenner and Beckmann (17) found quantum yields ranging from 1 at low pressures to 1.7 at higher pressures and hydrogen concentrations ranging from 58 to 64 per cent in the same pressure range of 2 to 14 mm., decreasing toward 50 per cent with increasing pressure.

The primary mechanism in hydrazine decomposition is still uncertain. If it be



then it would be necessary to fall back on reaction 6 to explain the ammonia formation observed. On the other hand, a primary mechanism



could by reaction 5 regenerate one-half the observed ammonia with the atomic hydrogen. The NH_2 and the N_2H_3 thus produced could, by several alternative mechanisms already proposed, but for which there is as yet no experimental test, yield $\text{NH}_3 + \text{N}_2 + \text{H}_2$ in approximate accord with the observations. The para-hydrogen conversion reaction might be employed to test these two alternative mechanisms for the primary photoprocess.

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SECONDARY PROCESSES IN THE PHOTOCHLORINATION OF CARBON MONOXIDE AND HYDROGEN¹

HUGH S. TAYLOR

Department of Chemistry, Princeton University, Princeton, New Jersey

Received May 25, 1938

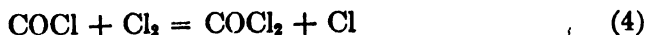
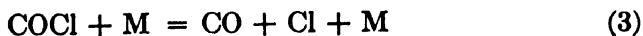
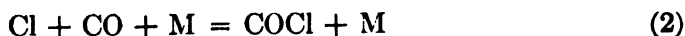
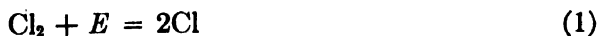
Since the publication of the Second Report of the Committee on Photochemistry considerable progress has been made towards a final and quantitative formulation of the secondary processes both in the hydrogen-chlorine combination and in the reactions, thermal and photochemical, of phosgene synthesis and decomposition. These several reactions have been the principal objective of the researches of Bodenstein and his school. At the present time Bodenstein (6) is occupied with the publication of the definitive conclusions of this long series of investigations and is attempting to incorporate within the framework of those conclusions, or reject for reasons ascertained, the auxiliary data that have accumulated from the investigations of other workers, notably Rollefson (15, 19, 20, 21), Ritchie (17, 18), Norrish (16), Allmand (1), and others. A discussion of the earlier work (3, 7, 8, 9, 10, 15, 22, 23, 24, 26) was included in the Second Report.

I. THE PHOSGENE REACTIONS

For the photoreaction at room temperatures and pressures over 100 mm. the kinetic expression is

$$\frac{d[\text{COCl}_2]}{dt} = \kappa_1 I_{\text{abs.}}^{1/2} [\text{Cl}_2][\text{CO}]^{1/2}$$

This equation is derivable from the Bodenstein reaction scheme:



¹ Contribution No. 9 to the Third Report of the Committee on Photochemistry, National Research Council.

Equations 2 and 3 lead, on the Bodenstein interpretation, to an equilibrium expressed by the equation:

$$K_{\text{COCl}} = [\text{Cl}][\text{CO}]/[\text{COCl}]$$

The first five reactions, with the assumed equilibrium, yield the kinetic expression for κ_1 , which is obeyed by experimental results, under the given conditions, except in the beginning of the reaction and towards the end when reaction 5' becomes important with low concentration of COCl . The same chain-ending process (5') becomes important also at higher temperatures and lower concentrations (< 90 mm.). At high temperatures the kinetic expression then becomes

$$d[\text{COCl}_2]/dt = \kappa_2 I_{\text{abs.}} [\text{Cl}_2][\text{CO}]$$

The reaction constants κ_1 and κ_2 are related by the following equations to the several constants of the individual reaction steps:

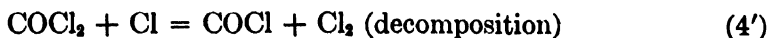
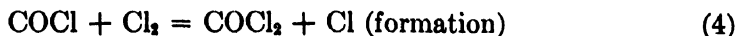
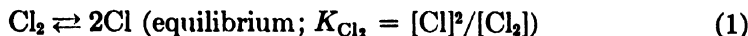
$$\kappa_1 = \frac{k_4}{k_5^{1/2} K_{\text{COCl}}}; \quad \kappa_2 = \frac{k_4}{k_5' K_{\text{COCl}}}$$

By reason of the additional investigations of Bodenstein, Brenschede, and Schumacher (4, 5), Bodenstein (6) has rejected the interpretation by Rollefson (19, 20), which makes use of Cl_3 as an intermediate, and maintains his contention that the COCl equilibrium exists in spite of reaction 4 in which this intermediate is steadily consumed.

The thermal formation and decomposition between 350° and 450°C . yield the kinetic expression

$$d[\text{COCl}_2]/dt = \kappa_{\text{th}} [\text{Cl}_2]^{3/2}[\text{CO}] - \kappa'_{\text{th}} [\text{Cl}_2]^{1/2}[\text{COCl}_2]$$

The reaction scheme pertaining to this is



The reaction constants κ_{th} and κ'_{th} are then given by the equations

$$\kappa_{\text{th}} = \frac{k_4 K_{\text{Cl}_2}^{1/2}}{K_{\text{COCl}}} \quad \text{and} \quad \kappa'_{\text{th}} = k_4' \cdot K_{\text{Cl}_2}^{1/2}$$

The numerical data for the equilibrium and reaction constants

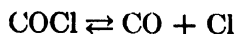
Bodenstein, Brenschede, and Schumacher (6) have recently completed a calculation of the numerical data for the several individual reactions and

for the equilibria involved. Their results are summarized in the following.

For the equilibrium between chlorine molecules and atoms the accurate data of Giaque and Overstreet (13) are available

$$\log K_{\text{Cl}_2} = \frac{57156}{4.571T} + 3.820$$

For the equilibrium



both the heat of reaction and the constant must be so chosen that

$$\log K_{\text{COCl}} = \log k_3 - \log k_2$$

Further, $\log k_3$ must be sufficiently greater than $\log k_4$ so that the assumption of practical equilibrium in spite of reaction 4 can be maintained. By trial, the equation obtained was

$$\log K_{\text{COCl}} = -\frac{5676}{4.571T} + 1.770$$

For reactions 4 and 5 the data are given in the form of equations

$$\log k = -\frac{E}{4.571T} + \log Z_1 + 1/2 \log T - \log f$$

where E is the activation energy, Z_1 the collision yield for $T = 1^\circ\text{K.}$, and f is the steric factor. In these equations E and f are both adjustable.

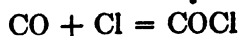
$$\log k_4 = -\frac{2612}{4.571T} + 1/2 \log T + 10.101 - 3.871$$

$$\log k_5 = -\frac{1940}{4.571T} + 1/2 \log T + 10.106 - 0.976$$

The equilibrium constant K_{COCl} yields the value 5676 cal. for the heat of formation of COCl . The heat of formation of phosgene from $\text{CO} + \text{Cl}_2$ is 26,100 cal. With these two data and the value of 2612 cal. from $\log k_4$ the expression for $k_{4'}$ becomes

$$\log k_{4'} = -\frac{23036}{4.571T} + 1/2 \log T + 10.110 - 0.171$$

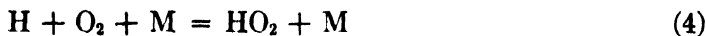
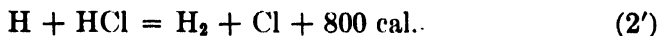
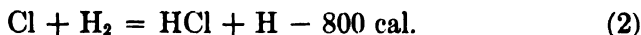
With these several equations the calculated values for the overall reactions, photochemical and thermal, from room temperatures to 450°C. agree excellently with the measured values. Bodenstein sees in this concordance the best and most convincing support for the reaction schemes assumed and for the equilibrium,



which Rollefson (19) especially has questioned. The heat of formation of COCl , 5676 cal., is materially lower than the value of 10 kg-cal. originally estimated, the higher figure justifying the objection of Rollefson. With the newer numerical data, Bodenstein is of the opinion that the several reactions are described very satisfactorily and, he believes, in final and definitive form.

II. THE HYDROGEN-CHLORINE PHOTOREACTION

The reaction sequence in the hydrogen-chlorine combination is, it is quite generally agreed, the Nernst chain mechanism, with the chains normally terminated by interaction of atomic hydrogen with oxygen impurities. The reaction scheme thus becomes



The numerical data for the several reactions are still subject to final revision but, according to Bodenstein, the most reliable data now available are obtained from the following equations for velocities, the units being in moles per liter per second.

$$\log k_2 = \frac{5750}{4.571T} + 1/2 \log T + 10.47 - 0.92 = 6.40 \text{ at } 288^\circ\text{K.}$$

$$\log k_2' = \frac{4950}{4.571T} + 1/2 \log T + 10.48 - 1.39 = 6.55 \text{ at } 288^\circ\text{K.}$$

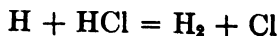
$$\log k_3 = -\frac{2550}{4.571T} + 1/2 \log T + 10.50 - 0.78 = 9.01 \text{ at } 288^\circ\text{K.}$$

$$\log k_4 = -\frac{500}{4.571T} + 1/2 \log T + 10.42 - 1.60 - \log f$$

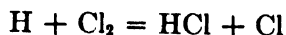
In the last expression the datum -1.60 represents the logarithm of the number of three-body collisions (moles per liter). The value of $\log f$ varies with M according to the best evidence. Bodenstein assigns the following values: $\log f = -1.37$ for $\text{M} = \text{Cl}_2, \text{H}_2, \text{O}_2$; $\log f = -0.77$ for $\text{M} = \text{HCl}$; and $\log f \sim -1.07$ for $\text{M} = \text{H}_2 + \text{Cl}_2$ mixture.

The value $E_2 = 5750$ cal. is obtained from Hertel's value for the temperature coefficient for $10^\circ = 1.37$. Hence, since $E_2 - E_2' = 800$ cal.,

E_2 becomes 4950 cal. From a comparison of

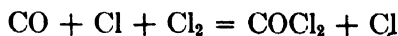


with

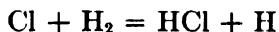


(in para-hydrogen) and the variation of k_2/k_3 with temperature, $E_2 - E_3 = 2400$ cal. and so $E_3 = 2550$ cal. From Hertel's data (14) it follows also that E_3 would be 2060 cal. if $\text{H} + \text{O}_2 + \text{M}$ were temperature-independent. To reconcile the two data for E_3 we therefore can set E_4 equal to 500 cal.

The absolute value of $\log k_2 = 6.40$ at 288°K. comes from a comparison, by Brenschede and Schumacher (4, 5), of



with



Hence $\log f = -0.92$. The absolute value of $\log k_4 = 8.60$, in the mean, was obtained by Bodenstein from analysis of data by Frankenburger and Klinckhardt (12) and by Bates (2) on peroxide formation from atomic hydrogen. From data of Ritchie (18), with experiments in which both water and hydrogen chloride were formed, $\log k_3 - \log k_4 = 0.41$ and hence $\log k_3 = 9.01$. The steric factor corresponding is then $\log f_3 = -0.78$. From Hertel's data already discussed $\log k_3 - \log k_2 = 2.46$. Hence $\log k_2$, at 288°K. is 6.55 and $\log f_2 = -1.39$. The uncertainty in the values for $\log k$ is estimated by Bodenstein to be not greater than 0.3.

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THE ACTION OF OPTICAL SENSITIZERS ON THE PHOTOGRAPHIC PLATE¹

G. KORNFIELD

Kodak Research Laboratories, Rochester, New York

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In this paper a survey is given of the published work dealing with the mechanism of optical sensitizing of photographic emulsions, the connection between sensitizing and other properties, and the mechanism of desensitizing. There are some facts available concerning the first point, and a close connection has been established between light absorption and sensitizing power. Up to the present time, however, only fragmentary information has been published on the relation between sensitizing power and other properties and on the nature of desensitizing.

I. INTRODUCTION

The spectral range of photographic action

Since photochemical action in any system is necessarily connected with its light absorption, the light absorption in silver halide emulsions is of fundamental importance for determining the spectral range of photographic action.

The absorption of pure silver bromide in a microcrystalline state was measured by Slade and Toy (1) in 1920. They found absorption beginning at about $450\text{ m}\mu$ which strongly increased towards the violet and ultra-violet regions. Eggert and Noddack (2), in 1923, found the limit towards the long wave length region at $465\text{ m}\mu$. In 1928 Eggert and Schmidt (3) undertook a very careful investigation of thin layers of microcrystalline silver bromide and silver chloride, for which they found the absorption limits towards the longer wave lengths, at $480\text{ m}\mu$ and $400\text{ m}\mu$, respectively. There is no limit towards the shorter wave lengths in pure silver bromide. Absorption and photochemical action occur throughout the whole ultra-violet region and beyond it. It is well known that the photographic plate was instrumental in Roentgen's discovery of x-rays. Photographic action, however, in this region of very large quanta is essentially different from that in visible and ultraviolet light. Glocker and Traub (4) found that, with x-rays, there was no threshold of sensitivity for small intensities,

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and Bunsen's reciprocity law was found to be valid over a long range. It is not to be expected that the law of photochemical equivalence will hold in the region of x-rays, where the photochemical action corresponds to the amount of energy transferred to secondary electrons. This was the conclusion from Glocker's (5) investigation in 1927. Eggert and Noddack (6) some time before had found that one quantum of x-rays absorbed corresponds to about 10^8 silver atoms released. That the law of equivalence does not hold in the x-ray region was also confirmed by Günther and Tittel (7). Between 0.245 \AA . and 1.54 \AA . the number of silver atoms per quantum absorbed changed from 920 to 148, but the ratio between the energy of the secondary electrons and the amount of reduced silver was found to be fairly constant.

The absorption of gelatin is negligible in the x-ray region, but, in the visible and ultraviolet regions, the presence of gelatin in the photographic emulsion distorts the close correlation between absorption and photographic action which can be observed in pure silver halides. Eggert and Noddack (2) determined the absorption of emulsion-coated plates in the region of the longer wave lengths and found more than 20 per cent absorption, even at $615 \text{ m}\mu$. This absorption is of no use in photography, however, since gelatin can not act as a sensitizer. In the far ultraviolet region gelatin actually impedes photographic action by its own strong absorption. For the region below $200 \text{ m}\mu$, therefore, Schumann plates, which do not contain any gelatin, are used.

Absorption is not so well defined in a photographic emulsion as it is in pure silver bromide. It is dependent, to some extent, on the mode of preparation. In an investigation with Frankenburger, Fajans (8) was the first to point out the deforming influence of adsorbed ions on the crystal forces which naturally must result in a spectral shift. In several succeeding investigations this spectral shift was thoroughly examined by him and his coworkers (9, 10, 11, 12, 13). Recently de Boer (14) has quantitatively connected the spectral shift with the heat of adsorption in the normal and excited state.

There is another factor which influences the absorption even more during exposure, that is, photolytically developed silver in colloidal form. The phenomenon was discovered as early as 1840 by E. Becquerel (15, 16) with a Daguerreotype plate (silver iodide on silver) which could be made sensitive to the yellow and even to the red region by long exposure. He observed the same effect with silver bromide and silver chloride papers. He therefore called the blue end of the spectrum "exciting radiation" and the yellow and red regions "continuing radiation". Lüppo-Cramer (17) and Eder (18), in 1909, explained the phenomenon as optical sensitizing by colloidal silver, and Lüppo-Cramer was able to reproduce the phenomenon by adding colloidal silver to silver chloride. The great extension

of the absorption region pointed clearly to the absorption of light by the colloidal silver and to its sensitizing property. This sensitizing property of colloidal silver, as well as of colloidal silver sulfide, in analogy to the organic sensitizing dyes was extensively considered by Sheppard (19).

In 1873 H. W. Vogel (20) discovered that some of the strongly absorbing organic dyes could be used as sensitizers for the photographic plate. Coral-lin was the first dye used by him to sensitize the plate for the yellow and green regions. He saw at once the significant correspondence between the absorption of the dye in solution and the sensitized region, although both regions do not coincide exactly, and he foresaw its practical importance. The value of this discovery can hardly be overemphasized, since panchromatic and orthochromatic plates were developed as a result, and the extension of photography during recent years far into the infrared region can be traced to its influence.

Most of the dyes which were employed as sensitizers in the beginning are now rarely used. At present nearly all the sensitizers used belong to the polymethine group, many of them being cyanine dyes. It is not intended here to describe in detail all the work that has been done on this subject. It ought to be mentioned, however, that close connections were found between the constitution of the dyes and their spectral range of absorption in solution. Once these connections were established, sensitizing dyes were synthesized for the whole visible region of the spectrum and through the infrared as far as $1356\text{ m}\mu$ (21).

The systematic connection, however, has been confined so far to the constitution of a dye, on the one hand, and the intensity as well as the region of its absorption, on the other. As yet no evidence has been found to connect its sensitizing property with its chemical constitution or with any other quality.

A great number of empirical facts on optical sensitizers have been found, but it seems hardly possible to fit them into a consistent picture. The conflicting results of earlier experiments can be explained partly by the fact that the sensitizers used were often not chemically pure and in some cases were even combined with various admixtures, but, even with pure materials, the complex nature of the phenomena makes it difficult to arrive at simple laws. Desensitizing was frequently regarded as optical sensitizing with a negative sign, and the difference in constitution was connected with this antagonistic behavior. It is only recently that desensitizing has been recognized as a property common to all sensitizers. It has been fairly well established, moreover, that sensitizing and desensitizing belong to different stages in the formation of the latent image and probably take place at different spots on the silver bromide grain. As early as 1907 Sheppard and Mees (22) made a very clear statement regarding the different stages for the action of sensitizers and desensitizers in the primary

process, but it seems generally to have been overlooked by other investigators. Then, in 1925, Sheppard (23) emphasized the fact that desensitizing does not produce any detectable shift in the spectral sensitivity. One year later von Hübl (24) stated quite clearly that, for a special spectral region, a desensitizer might as well be considered also an optical sensitizer, since both actions were not connected with each other, optical sensitizing depending on color, whereas desensitizing as a chemical reaction can be produced by colorless substances. In 1931, writing on "Sensitizing by Desensitizers", Lüppo-Cramer (25) stated that it seemed futile to divide the dyes into sensitizers and desensitizers, since the same dye might belong to either class, according to the conditions under which it was used. He supported this statement by several facts: (1) Many dyes known as optical sensitizers in silver bromide emulsions act as desensitizers in silver iodide emulsions. (2) If an acceptor for halogen is added to a silver bromide emulsion, many dyes known as desensitizers then act only as sensitizers. (3) To unripened emulsions some desensitizing dyes (Capri blue, Janus green) act as sensitizers when used in low concentrations.

A very cogent argument in favor of the above statement is the existence of optimum conditions for the sensitizing baths regarding concentration and time of bathing. This fact was discovered by Sheppard (57) as early as 1908 with a solution of an isocyanine dye. In 1933 Heisenberg (26) showed for three dyes, namely, pinacyanol, thiocarbocyanine, and selenocarbocyanine, that there is an optimal concentration for the adsorption of a sensitizing dye, at which nearly all the dye is adsorbed. With concentrations increasing beyond this optimal concentration, desensitizing sets in, and Heisenberg proved that this desensitizing effect is real, since it is much too large to be accounted for merely by the increased light absorption of the dye. This desensitizing effect of sensitizing dyes when used in larger concentrations seems to be of a general nature. A very extensive and careful recent investigation by Leermakers, Carroll, and Staud (27) showed invariably the same result.

The desensitizing action, then, is to be considered a property common to all optical sensitizers and, although this statement is not reversible, because desensitizing is not exclusively a property of optical sensitizers, a study of desensitizing should contribute something to the knowledge of optical sensitizers. The connection, however, between the specific character of a sensitizer and its desensitizing property if used in excess is a little more remote than that with optical sensitizing which will, therefore, be dealt with first.

II. SENSITIZING ACTION

A. *The sensitizing process*

The sensitizing action has always been believed to be closely connected with the primary act of absorption, and quite recently Leermakers (28) has

confirmed very accurately the close correspondence between sensitivity and absorption in a sensitized emulsion. The conclusion thus seems inevitable that sensitizing is connected with the primary act of light absorption. Now, according to the present state of the theory of the latent image, into which Webb (29) has introduced quantum mechanics, absorption in unsensitized silver bromide results first in the raising of an electron to a higher level. In this level its mobility is not blocked by other electrons and, accordingly, photoconductance results. This photoconductance was measured by Toy and Harrison (30) and was found within 0.07 sec. to reach a stationary state which was proportional to the intensity. This would be expected if the majority of the electrons left the upper level again and dropped to a lower level. It has been assumed that such lower levels are produced by impurities and that in catching the electrons they give rise to the color centers, which are called F centers, in Pohl's terminology. Hilsch and Pohl (31) found in crystals of alkali halides that these F color centers are characterized by sharp absorption bands; in silver halide crystals, the absorption bands are more diffuse and broader, overlapping the proper absorption of the silver halides. Hilsch and Pohl assume that it consists of various bands belonging to different states of aggregation, since there is evidence that, in the silver halides, the photoproduct collects into specks of varying dispersity immediately after it is formed. In this connection it is perhaps of some interest to point to the results of Wagner and Beyer (32). They found that the lattice defect in silver bromide crystals is produced by interstitial silver ions which have left their normal places in the lattice, whereas in alkali halides the ions which have left their places are not present in the lattice any more. For the photographic emulsion Sheppard (23) stressed the necessity of dividing the formation of the latent image into two stages: (1) the primary act of absorption and (2) the formation of concentration specks around the sensitivity specks. He was able to show that the relative spectral sensitivity was scarcely affected by the formation of sensitivity nuclei (such as from thiocarbamide), which greatly increased the absolute sensitivity to any wave length, and Carroll and Hubbard (33) confirmed this statement. Webb has pointed out that the results obtained by Pohl and his school, in crystals, fit very well into the concentration-speck hypothesis suggested by Sheppard, Trivelli, and Loveland (34) for the photographic emulsion. Recently experimental evidence has been found for the existence of such concentration centers in photographic emulsions. Van Kreveld and Jürriens (35) devised an extremely sensitive method for measuring the absorption of a photographic plate after exposure. They found that the characteristic absorption between 5900 Å. and 7000 Å. was proportional to the time of exposure (36). The intensity of absorption taken as a function of the time of exposure gave a straight line passing through zero. Moreover, the method was so sensitive that they could include very short

exposures in their measurements. The first point was produced by an energy of 9×10^{11} quanta per cm^2 on an Ilford Process plate. This point actually lies at the beginning of the overexposure region of the H. and D. curve, but is still so near to the region of the latent image that there is a high probability that the latent image is characterized by the same absorption.² Now the same absorption, only increased in intensity, has also been found for the print-out region, in which Eggert and Noddack (37) found the amount of photolytically produced silver to be that required by the law of photochemical equivalence. They also extrapolated their results to the region of the latent image, and the investigations of van Kreveld and Jürriens confirmed their statement. It can be assumed, therefore, with a probability very near to certainty, that the latent image consists of silver which has been produced by light according to the law of photochemical equivalence, so that, for each electron released, one atom of silver is formed.

In a sensitized emulsion the same primary process is supposed to take place, but with one exception. The original level from which the electron is raised is higher than the original level in the unsensitized emulsion and, accordingly, the energy required for raising it is less. Sheppard and Crouch (38) attributed this electron level to the sensitizing dye, and this assumption seems amply justified by the close resemblance between the absorption spectrum of the sensitized emulsion and that of the sensitizing dye itself. Thus, in the sensitized region, the electron should originate from the adsorbed dye, whereas, in the absorption region of silver bromide, it should originate from the bromide ion in the lattice. One more fact should be mentioned as an argument in favor of this theory, i.e., the photoconductance of sensitizing dyes. As early as 1905 Joly (40) pointed out the parallelism between photoconductance and absorption in sensitizing dyes, and in 1923 Zehodro (41), in comparing the photoconductance of three sensitizing dyes (cyanine, pinaverdol, and pinachrome) in dry collodion, with their absorption, found complete correlation. This result, however, is not conclusive. The photoconductance of the dyes should be investigated in the same specific molecular state in which they are adsorbed in the silver bromide emulsions.

From the theory just outlined it should be concluded that not more than one silver atom could be produced by the light-action of one dye molecule unless this molecule could be restored to its former state, rather than be decomposed after the release of an electron. This assumption seems far-fetched, although one fact points in this direction,—the strong fluorescence which is found in sensitizing dyes. It is to be regarded, however, as one of the possible solutions for a puzzling experimental result

² It must be borne in mind, however, that it would hardly be possible to discover a slight deviation of the straight line in the region of the latent image.

obtained by Leszynski (42), by Tollert (43), and recently by Bokinik and Iljina (44).

All these authors found that, in a sensitized emulsion, the number of silver atoms present after exposure was many times greater than the number of dye molecules. Leszynski found that, after the exposure of an emulsion sensitized by erythrosin, the ratio of silver atoms to dye molecules was of the order of 20. Tollert repeated Leszynski's investigation with a very fine-grained emulsion, taking care to consider only those dye molecules which had actually been adsorbed to the silver bromide, and arrived at the same result. With the dye concentrations and exposure times which were used in his experiments, a ratio of 64 was actually found. Both authors used the same analytical methods and there is a possibility, of course, that a systematic error could have been made which is responsible for the anomaly. The method used was the same as that of Eggert and Noddack (37), i.e., first dissolving the silver bromide in thiosulfate and then determining the amount of silver in the precipitate. The thiosulfate might have given rise to some silver sulfide which would increase the amount of silver in the precipitate. There is always a tendency for thiosulfate to give silver sulfide, especially in the presence of gelatin, and this might be increased by the presence of the dye.

There is, however, additional evidence for a high, although not equally high, efficiency of the sensitizing dyes, namely, the work of Bokinik and Iljina (44). These authors investigated the sensitizing action of erythrosin in silver bromide sols without gelatin and with an excess of bromide ions, with the result that the ratio of silver atoms to adsorbed dye molecules was found to lie between 4 and 15, rising with increasing alkalinity. It appears, however, that some other spectral region than the green light of the sensitizing region enhanced the effect on the silver bromide sol, for, if their curves (amount of silver against adsorbed dye) are extrapolated to a dye concentration of zero, a large and varying amount of silver seems to have been formed in every case.

Thus, although the results of all three experiments are not quite conclusive, still they are not to be considered wrong.³ Accordingly an explanation for the results should be sought. Three different explanations have been offered, one of which has already been given, i.e., that the dye molecule is restored after the release of an electron. This restoration of the molecule could easily occur if the remaining part did not decompose in the meantime. In this connection, a study of phosphorescence in adsorbed dyes would be of interest.

Another explanation is the possibility that the absorbing dye molecule

³ These results were strongly supported by an experiment recently reported by Dr. Sheppard at the September, 1937, Meeting of the American Chemical Society, which will be referred to later in this paper.

imparts its energy somehow to the crystal lattice, so that an electron is released from the lattice and the dye molecule is not affected at all. This is the explanation preferred by Leermakers (28), but it does not explain why the energy required to release an electron in the silver halide lattice should be reduced to such an unusual degree by the adsorbed dye, nor why this energy should correspond so closely to the absorption of the dye itself. Recently Scheibe (44a) has tried to find a solution for this question by assuming that the dye in an aggregated state should be able to absorb more than one quantum in one elementary act.

There is a third explanation connecting the excess of silver atoms over dye molecules with a chemical reaction of these latter molecules. Sheppard and Crouch (38) suggested an explosion of the dye molecule after the release of an electron, and they produced experimental evidence for the occurring of a chemical reaction between cyanine dyes and silver halide in the presence of light. Other contributions to this question have recently been made by Semerano (45, 46) and by Mecke and Semerano (47). The most recent results of Sheppard, Lambert, and Walker (46a), however, referred to already in this paper, rule out this explanation, for these authors were able to show that in the presence of an acceptor for halogen the sensitizing action proceeds without any decomposition of the dye. Thus the decomposition of the sensitizing dye can not be connected with the actual sensitizing. The part played by the sensitizing dyes in the photographic process seems, on the whole, to be fairly well established, although some questions remain still to be answered.

The main problem, however, concerns the properties which are required to make a sensitizer out of a dye, and unfortunately very little is known about them. In the following sections a survey will be given of the attempts which have been made to correlate the various properties of dyes with their sensitizing characteristics.

B. Adsorption of sensitizers

The fact that adsorption is a necessary though not a sufficient condition for sensitizing has been known for some time (22). As early as 1904 Kieser (48) studied a great number of sensitizing dyes in their relations to the surface of silver halide grains, and found that saturation was reached at very low concentrations of the dye, but it was only recently that quantitative measurements were started of the adsorption of sensitizing dyes by silver halide emulsions.

In 1925 Sheppard and Crouch (38) measured the adsorption of Orthochrome T, dissolved in water, on a silver bromide emulsion with only 1 per cent gelatin at 50°C. The adsorption was measured in two ways: (1) by extracting the aqueous solution of the remaining dye with chloroform and determining the dye concentration with a spectrophotometer, and (2)

by determining directly the amount of dye adsorbed at the silver bromide grains after dissolving them in thiosulfate. The results of both methods agreed fairly well. The adsorption curves at first showed increasing adsorption with increasing concentration. Then, over a large part, the curves were parallel to the concentration axis until finally they rose steeply again with further increase in concentration. The parallel parts of the curves were interpreted by the authors as representing saturation in a single layer, and the steep rise afterwards was assumed to be due to the agglomeration of multilayers. The size-frequency of the silver bromide grains was measured, and the surface area was calculated and compared with the amount of adsorbed dye in a saturated single layer. This latter value varies according to the alkalinity. For a pH of 5.5 there were found 5×10^{-10} gram-moles of dye per square centimeter of surface area. According to a statement of Trivelli and Sheppard (49), the authors assumed the surface area to consist mainly of bromide ions, since excess bromide was present. By calculating the number of bromide ions in the surface, they were able to establish the ratio of bromide ions to dye molecules as 2.3. In connection with the adsorption at bromide ions, the increase of adsorption in alkaline solutions presented some difficulty. For, although it would have seemed natural to assume that the dye cations were adsorbed at the bromide ions, the increase in adsorption in alkaline solution pointed to the adsorption of the molecular form. There were two forms of the dye found in a solution in water, a dissociated uncolored form which was soluble in water, and an undissociated colored form which tended to be dispersed in colloidal solution in water (50), whereas, in alcohol and other organic polar solvents, the colored form was more soluble. The equilibrium between these two forms in water depended on the acidity. The dissociated colorless form prevailed in acid solution and the colored form in alkaline solution. Thus it seemed certain that the colored form, although not actually dissociated, was still exclusively adsorbed at the bromide ions. A parallel may be drawn, perhaps, to the statement of Franck and Eucken (51), according to which energy exchange is facilitated between molecules which can react with each other, even though they can not react under the special conditions under consideration.

The connection between the basic or acid nature of a dye and the place of adsorption in silver bromide was confirmed in an investigation by Sheppard, Lambert, and Keenan (52). The acid dye dichlorofluorescein was found to be adsorbed only in the presence of an excess of silver ions, whereas, in alkaline solution, the basic dye pinacyanol was adsorbed only at the bromide ions. It should be mentioned here that the experimenters of Leermakers, Carroll, and Staud (39) gave the same results. All the basic cyanine dyes were adsorbed exclusively by the bromide ions. An investigation of the adsorption of pinacyanol (52), carried out parallel with the

investigation of the adsorption of Orthochrome T, yielded a value between 1.69 and 2.78 for the ratio of bromide ions to dye molecules. (The range of variation depends on the assumption of octahedral or of cubic faces at the surface.) This value was found to be roughly in agreement with the results of other investigations, on dye adsorption at silver bromide surfaces, which had been carried on in the meantime. Having found eight bromide ions for one molecule of adsorbed methylene blue, Wulff and Seidel (53) collected other data on adsorption at the surface of salts of heavy metals. They gave the ratio 3 as the result of an experiment on the adsorption of erythrosin at silver bromide surfaces carried out by O. J. Walker and K. Fajans.

Since that time other investigators have very definitely confirmed the ratio $\frac{\text{Br}^-}{\text{dye}} > 1$. Bokinik (54) gave the ratio 10 for pinacyanol, and Leermakers, Carroll, and Staud (27) found the ratio 10 for two different thiocarbocyanines and 20 for a thiodicarbocyanine. Their saturation value was defined as the amount of dye adsorbed at optimal sensitization, whereas saturation in Sheppard's experiment was defined by the parallel part of the adsorption curves. Since both methods yielded different results (the ratios being 2 and 10, respectively), the authors concluded that there exists a difference between saturation considered from the point of view of adsorption, and saturation considered from the point of view of sensitizing. Their investigation was a systematic study of the correlation between the optimal concentration of a sensitizer and the available grain area, and it was carried out with three different dyes and seven emulsions. The curves obtained by plotting the sensitivity in various spectral regions against the logarithm of the dye concentration show a great increase in sensitivity towards the optimal concentration in the red region, a slighter increase in the green part of the spectrum, and no change in the blue part. At higher concentrations a decrease in sensitivity occurs throughout the whole spectrum. At the optimal concentration, practically the whole amount, i.e., 99 per cent, of the dye was found to be adsorbed. For concentrations beyond this the percentage of unadsorbed dye increased rapidly. (For pinacyanol, thiocarbocyanine, and selenocarbocyanine, Heisenberg (26) obtained exactly the same results.) The surface area for each emulsion was determined from the projective area of the average grain, the number of grains per cm^2 , and the volume of the average grain (obtained by finding the silver content of the emulsion, the density of silver bromide, and the number of grains). The results are shown in table 1 (taken from the paper by Leermakers, Carroll, and Staud (27)).

The fifth column shows a remarkably constant value for each dye. This constant ratio of adsorbed dye to available surface is especially remarkable, since the emulsions were prepared in various ways, both from neutral

silver nitrate and from ammoniacal silver oxide. Discussing the difference in the ratio, dye to surface, for dye I and dye II, on the one hand, and dye III, on the other, Leermakers, Carroll, and Staud point out that the deviation is in the right direction, since dye III as a thiodicarbocyanine has a larger area than dye I or dye II, both of which are thiocarbocyanines. They point out at the same time, however, that the deviation is greater than could be accounted for by the difference in size. The data of table 1 are used to estimate the amount of surface saturation at the optimal concentration. For dye II, an 8-alkylthiocarbocyanine, the surface is assumed

TABLE 1
Optimal surface concentration of sensitizing dyes
(From Leermakers, Carroll, and Staud (27))

EMULSION	SURFACE <i>cm.² per cm.³</i>	DYE	OPTIMAL CONCENTRATION <i>moles per cm.³ of emulsion $\times 10^8$</i>	MOLES OF DYE PER CM. ² OF SURFACE $\times 10^{11}$
1	400	I	3.6	9.0
2	480		3.8	7.9
3	580		5.2	9.0
4	660		6.0	9.1
5	840		7.2	8.6
6	950		9.0	9.4
7	1080		12.0	11.1
1	400	II	4.4	11.0
3	580		6.3	10.9
4	660		8.0	12.1
6	950		11.2	11.8
7	1080		12.6	11.6
1	400	III	1.9	4.8
3	580		2.3	4.0
4	660		2.9	4.4
6	950		4.8	5.0
7	1080		4.8	4.4

to be 150 Å., according to the values given recently for atomic radii. If the molecules are assumed to lie flat on the crystal surface, they will then cover $11.5 \times 10^{-11} \times 6 \times 10^{23} \times 150 \times 10^{-16}$ cm.² per square centimeter of surface, or 1 cm.² per square centimeter, i.e., they will form a unimolecular layer.

This result seems fairly convincing, although the authors themselves are willing to assume that it may be a coincidence, because there are other facts (39) which seem to require the assumption of an agglomeration of the adsorbed dye. These data are connected with some spectral characteristics which will be reported later in the present paper.

Two more investigations should be mentioned in connection with adsorption measurements,—one by Bagdassarjan and Rabinovitch (55), and the other by Ščetinkina (56), which was reported by Rabinovitch. Bagdassarjan and Rabinovitch, studying the adsorption isotherms of silver bromide suspended in water, of erythrosin, eosin, rhodamine B, pyronine G, phloxine, acid rhodamine, and Bordeaux B, and their sensitizing power in silver bromide emulsions, found again that adsorption was necessary for sensitizing. In addition, they discovered that dyes (pyronine G) with adsorption isotherms which do not show any flat portions pointing to saturation are extremely weak sensitizers. Ščetinkina (56) measured the dependence of sensitizing action on the concentration of the sensitizer, and found a maximum for erythrosin and phloxine at relatively low concentrations. At very high concentrations the sensitivity decreases. These results are in good agreement with the results of the other investigators.

C. Some special spectroscopic properties of sensitizers

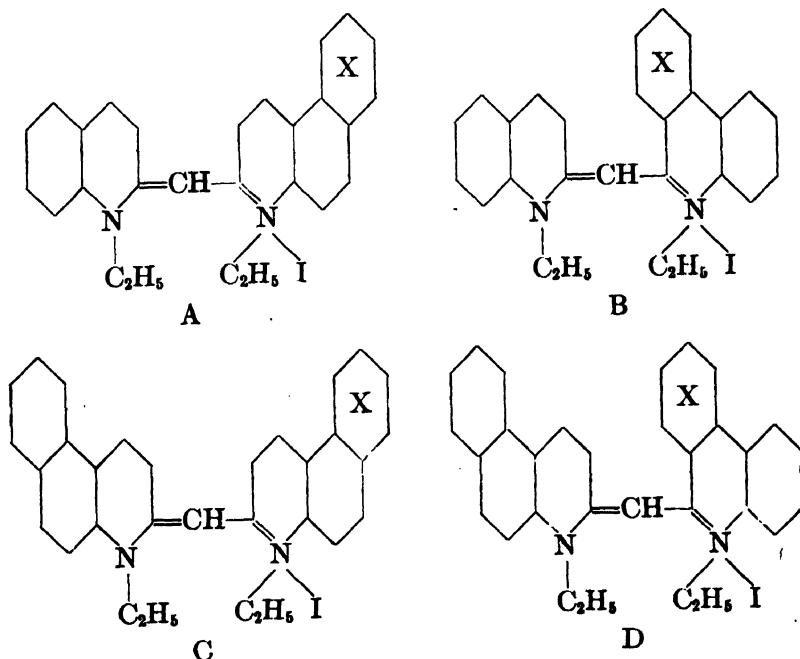
That the absorption spectra of dyes vary according to the solvent has been known for a long time. In 1908 Sheppard (57) investigated the absorption of some sensitizing dyes in alcoholic solutions and in water and found a very marked difference between them. The sensitivity curves of emulsions sensitized by these dyes resembled to some extent the absorption curves in water. In another investigation Sheppard (50) obtained some ultramicroscopic evidence of the colloidal state of the dyes dissolved in water. Recent investigations of this were carried on by Scheibe (58), by Scheibe, Kandler, and Ecker (59), by Scheibe, Mareis, and Ecker (60), by Jelley (61, 62), and by Leermakers, Carroll, and Staud (39).

A peculiar spectroscopic phenomenon, discovered by Jelley for a special cyanine dye (1, 1'-diethylpseudocyanine chloride), was observed when the dye was changing from true solution in alcohol or a similar solvent to the crystallized state. During the change it passed through a transitory state characterized by a sharp absorption band at about 575 m μ . This absorption band was associated with a strong resonance fluorescence, an unusual phenomenon in the liquid or solid state. This transitory state of the crystal was found to be relatively stable in solutions of some salts and in the case of adsorption of the dye on various substances (59).

In investigating silver bromide emulsions sensitized by cyanine dyes, Leermakers, Carroll, and Staud found similar sharp characteristic absorption bands for many adsorbed dyes. It was this fact which made them doubtful of the unimolecular layer, since Scheibe, Kandler, and Ecker attributed these spectral characteristics to a polymerized state, and Scheibe, Mareis, and Ecker confirmed this statement. Jelley, however, assumed a nematic state, i.e., a liquid crystal with orientation along one

axis only, and the question of the "aggregated" state was left open.⁴ Whatever this state be called, it will still be tempting to link it with the sensitizing power. But some of the results of Leermakers, Carroll, and Staud are not in agreement with the assumption that the sensitizing action is exclusively a property of this "aggregated" state. They found parallelism between sensitivity and absorption in all spectral regions, not merely for the bands belonging to the nematic state, but also for bands in other spectral regions which were obtained in emulsions dyed from alcoholic solutions. The sensitivity, however, was always proportional to the absorption.

Another connection seems worth investigating, namely, that between fluorescence and sensitizing, especially with regard to the possibility (mentioned in the discussion of the sensitizing process) that the dye molecule could be quickly restored after the release of an electron. Fluorescence in solutions is known to occur very frequently in cyanine dyes (63), but it is important to know whether the dyes adsorbed to silver bromide will show fluorescence. An investigation of the fluorescence of sensitized emulsions would be especially interesting in view of some remarkable results obtained with isomers by Brooker and Keyes (64) and by Leermakers, Carroll, and Staud (39). These isomers have the following constitution:



⁴ At a recent meeting (September, 1937) of the American Chemical Society Dr. Sheppard suggested a unimolecular layer in which the molecules are standing on edge, so that aggregation could take place in one dimension.

The only difference between A and B, or between C and D, lies in the position of the benzene ring marked X. Each of the dyes showed strong adsorption to silver bromide emulsions and a sharp absorption band, but only A and C were found capable of sensitizing the emulsions; B and D did not act as sensitizers. It would be interesting in this connection to know whether the isomers show any differences in fluorescence or photoconductance.

There are at present very few data which can be attributed to the sensitizing property. Bokinik (65) points out, in discussing the various explanations offered for the sensitizing action, that, of all the existing dyes, only those related to the phthalein or the cyanine groups were found to be sensitizers, but this statement is more applicable to the properties desirable for a practically useful sensitizer than to the sensitizing property itself.

Chibisoff (66), on the other hand, calls attention to some secondary effects of optical sensitizers whereby they act simultaneously as chemical sensitizers. These effects are especially marked when the dyes are added to the emulsions before ripening. They can then influence the growth of the crystal and the ripening process. Bancroft, Ackerman, and Gallagher (67) have connected the sensitizing power of a dye with its reducing action as an acceptor for halogen, and accordingly define an optical sensitizer as a dye which absorbs light in a special region and which is capable of reducing silver salts.

III. DESENSITIZING ACTION

The desensitizing action, as a property common to all sensitizers at high concentrations, should reveal some information on their characteristics. Unfortunately, the phenomenon itself seems complex, and the variation of terminology with author and time has helped to confuse the picture still more. There is, however, one fact which seems to be fairly well established: namely, that desensitizing takes place at the developing centers and not at the places of primary absorption (68). In addition to many facts which lead to this conclusion, there is an experiment reported by Lüppo-Cramer that definitely proves this point. Pinakryptol yellow is a very strong desensitizer and is even capable of dissolving the silver of the print-out image (70, 71). Accordingly, no darkening was observed in developing a plate which had been desensitized with pinakryptol yellow before exposure, but after dissolving the silver bromide in thiosulfate, the plate could be developed physically. This demonstrates clearly that the primary act of absorption during exposure was not impeded by the desensitizer adsorbed at the surface.

According to this result Weber's theory (72, 73) can be rejected, in so far as optical sensitizers are concerned. His theory assumed that desensi-

tizing has only an indirect influence on silver bromide by removing the optical and chemical sensitizers. This was supported by the following facts: Lüppo-Cramer (74) showed with many examples that emulsions of silver bromide in collodion were not susceptible to the action of desensitizers unless they contained a sensitizer. Mudrovčič observed that cyanine dyes and the desensitizer methylene blue reacted with each other. In water and in collodion the cyanine dye was bleached out in the presence of methylene blue. (Since, however, in gelatin the process was reversed, the methylene blue being destroyed, this effect could as well be used as an argument against Weber's theory.) Finally, Weber himself observed that, in a sensitized plate, desensitizing showed more strongly in the sensitized spectral region than the absorption region of silver bromide. Blau and Wambacher (76) strongly objected to accepting this as a general statement and pointed out that, wherever this secondary effect was found, it could be easily explained by preferential absorption of the desensitizer.

It would indeed be difficult to explain by this theory the desensitizing effect of optical sensitizers at high concentrations. With regard to the assumed effect of desensitizers on chemical sensitizers contained in gelatin, by which Weber explained the difference between gelatin and collodion in regard to the susceptibility to desensitizing, Blau and Wambacher pointed out that this explanation could not be valid. For, in the meantime, Ollendorff and Rhodius (77) had succeeded in coating plates with a silver bromide emulsion without any protective colloid which could be desensitized with methylene blue. Lüppo-Cramer confirmed (78) this result, although he did find that the number of dyes capable of acting as desensitizers is much more limited in such colloid-free emulsions. Even pinakryptol yellow, one of the strongest desensitizers, is ineffective with them. The exceptional susceptibility to desensitizing was explained for the gelatin emulsion by Lüppo-Cramer as being related to the high degree of dispersion of the latent image in gelatin.

In a special case there would, of course, always be the possibility of a complication by some of the secondary effects which have just been discussed, but desensitizing as a general phenomenon can safely be taken as a direct action on the developing centers. Even so, the range of possible reactions is still very wide and many questions remain to be answered.

There is the Herschel effect, i.e., the simple regression phenomenon produced by infrared radiation (the name, "Herschel effect," is used here for the direct regression, as it was used originally, i.e., the "visible" Herschel effect, as named by Trivelli (80)). Does desensitizing mean sensitizing of the Herschel effect? Or is it merely an oxidation of the silver in the latent image? Is it essentially an isolation of the developing nuclei (68)? Does it merely prevent the formation of the latent image,

or does it also destroy it? Is the desensitizing action merely a "narcosis" (81) of the centers lasting through development? And are these reactions influenced by light absorption?

Some of these questions can be answered from the results of various investigators. Some significant results have been obtained by Sheppard (82) concerning the mechanism of reaction on the silver bromide grain. By measuring the electromotive force in concentration cells with silver salts, he found a strong tendency to form complex silver salts in several compounds used in photography either as sensitizers, desensitizers, or antifogging agents.

It is conceivable that complexes are formed with silver either *in statu nascendi* or in the very fine dispersion of the latent image when oxygen is present. In experiments by Blau and Wambacher it was found that, for desensitizing at least, oxygen was necessary, unless there was an excess of chloride ions (83, 84, 85). Pinakryptol yellow, induline scarlet, antilumine, and phenosafranine did not act as desensitizers when oxygen was completely removed, either by evacuation or by substituting nitrogen.

The strong influence of halide ions on the desensitizing action had previously been observed by Carroll and Kretchman (86). With safranin either the sensitizing or the desensitizing effect was found, depending upon the concentration of bromide ions. The investigation of Carroll and Kretchman rendered quantitative results on the influence of light on desensitizing, and they were able to show the good correlation between reversal and energy absorption. This reversal phenomenon is, of course, not related in any way to the well-known photographic reversal, the beginning of solarization. The reversal by desensitizers can be identified with the "latent Herschel effect" as Trivelli named it, contrasting it to the "visible Herschel effect", which is a direct regression of the print-out image and which was, in fact, the effect actually discovered by Herschel. Where the regions of absorption by silver bromide and the dye were sufficiently separated in wave length, maxima were found corresponding to each region. Desensitizing can, therefore, be considered as a reaction in the developing centers which can be photosensitized by the light absorbed either by silver bromide or by the desensitizing dye. The photosensitizing is not the only reaction produced by a desensitizer. Loss of developability occurs also in the dark, but at a much lower rate. This was demonstrated by Carroll (87) and confirmed by Mauz (88).

There still remains the question of whether desensitizing involves destroying the silver centers or merely making them unfit for development. Or rather, it should be asked whether there are any desensitizing dyes which impede the development of the silver centers without destroying them. For, quite aside from the dyes (such as methylene blue, Janus green, etc.) which are known to be capable of dissolving silver (89), there is pinakryptol

yellow, which was found by Hübl (90) to be capable of preventing the formation of a print-out image. Lüppo-Cramer had shown that the dye can even destroy the print-out image (70). Tollert observed that a plate desensitized with pinakryptol yellow yielded a smaller amount of photo-lytically formed silver than a plate which had not been desensitized. If this experiment were repeated with other desensitizers, the question mentioned above could be answered. With a colorless desensitizer it could even be done in a region much nearer that of the latent image, since van Kreveld and Jürriens (35) have developed a method of determining the latent image by measuring the absorption in the red region of the spectrum.

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PHOTOSYNTHESIS¹

WINSTON M. MANNING

Wisconsin Geological and Natural History Survey, Madison, Wisconsin

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I. INTRODUCTION

In this review major emphasis will be placed on the photochemical and kinetic aspects of photosynthesis. The influence of the various physiological factors is more fully discussed in other recent reviews of photosynthesis (23, 24, 58, 72).

Except for studies of the physical and chemical properties of extracted plant pigments, investigations of photosynthesis are practically limited to a study of living plants. This limitation introduces complications not found in non-biological photochemical studies. In the first place, other chemical reactions, thermal as well as photochemical, undoubtedly occur during a period of photosynthesis. Unless proper allowance is made, these reactions may be of sufficient magnitude to obscure the significance of the photosynthesis measurements. In the second place, variations in factors influencing photosynthesis must be limited to those which will not kill or seriously injure the plant during the time when measurements are being made. In many cases, moreover, a variation in a particular environmental (external) factor may influence photosynthesis indirectly through its effect in the plant on internal factors other than those directly connected with the photosynthetic mechanism. This is particularly true for experiments with the higher plants.

Emerson (23) has discussed more fully some of the limitations involved in photosynthesis research.

II. THE MEASUREMENT OF PHOTOSYNTHESIS

Only a brief outline of experimental procedure will be given here. More extensive descriptions of the earlier methods which have been employed may be found in the monographs of Spoehr (70) and Stiles (74). Details of later procedures may be obtained from the original papers.

Photosynthesis is usually measured by determining either the amount of carbon dioxide consumed or the amount of oxygen liberated, or both.

¹ Contribution No. 11 to the Third Report of the Committee on Photochemistry, National Research Council.

Less direct methods may also be used, such as the measurement of the change in dry weight or sugar content of the plant material under investigation. However, results so obtained may involve factors other than the photosynthetic process.

The measurement of photosynthesis in land plants

With land plants photosynthesis may be measured by using either an entire plant or only part of the plant (often a single leaf). When a single leaf is studied, it is often detached from the rest of the plant, although many recent investigators have worked with attached leaves (41, 59, 60). In either case the material to be investigated is usually enclosed in a light-transmitting chamber.² The change in carbon dioxide or oxygen composition during a period of illumination or darkness may then be determined. In practice a flow method is often employed in order to maintain a nearly constant carbon dioxide concentration in the reaction chamber.

The change in gas composition during a period of darkness gives a measure of respiration. It is usually assumed that, for a given temperature, this process proceeds at the same rate in light as in darkness. A correction for respiration is therefore made in calculating absolute photosynthetic rates.

The change in oxygen and carbon dioxide may be determined by gas analysis (17), but other methods, in which only carbon dioxide is determined, are more frequently used.

In the conductivity method (43, 59, 60, 71, 76), the carbon dioxide is absorbed by a solution of alkali at constant temperature ($\pm 0.01^\circ\text{C}$). The conductivity of the hydroxide-carbonate mixture gives an accurate measure of the amount of carbon dioxide absorbed. With this method a continuous record of photosynthetic (or respiratory) rate may be obtained. Thomas and Hill (76) constructed a chamber large enough to enclose a field plot of wheat or alfalfa plants 6 feet square, and used the conductivity method to obtain a continuous record of photosynthesis and respiration, the measurements sometimes extending over a period of several weeks.

Instead of measuring the conductivity of the hydroxide-carbonate mixture, some investigators have titrated the mixture with standard acid (41). This method requires less apparatus than the conductivity method, but it is not as suitable for continuous measurements.

McAlister (53) has recently developed a very sensitive spectrometric method for determining carbon dioxide. This method is well adapted for continuous measurements of photosynthesis in land plants. A closed

² In single leaf studies the chamber may be attached to the under side of the leaf, with the leaf forming part of the chamber wall (41, 60). This permits nearly normal air circulation and transpiration.

system is used, with the gas rapidly circulating through the plant chamber and through an optical absorption tube. The absorption by the 4.2–4.3 μ band of carbon dioxide is determined with a rock salt spectrograph and a vacuum thermocouple. A notable characteristic of this method is its rapid response to changes in photosynthetic rate.

Photosynthesis measurements in algae and other aquatic plants

Photosynthesis measurements in aquatic plants are usually carried out with the plant material suspended in water. However, both van den Honert (77) and van der Paauw (78) have worked with moist films of *Hormidium* (a very small filamentous blue-green alga) attached to glass plates. The rate of oxygen evolution by the suspended plant material is usually used as the criterion of photosynthetic rate.

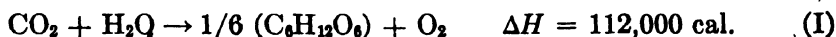
The manometric method of Warburg (84) has been widely used for measuring changes in oxygen concentration in experiments with aquatic plants. In this method the plant material is suspended in a carbonate-bicarbonate buffer mixture (usually about 0.1 molar), and placed in a closed glass vessel connected to a manometer. The buffer concentration is high enough to maintain a practically constant carbon dioxide partial pressure in the gas phase, so that the increase in gas volume due to oxygen evolution can be read directly on the manometer. Vigorous shaking is necessary to maintain equilibrium between gas and liquid phases. With some modifications the manometric method can be applied to measurements carried out with an unbuffered nutrient solution (9, 85). This modification requires the use of two vessels and depends upon the difference in solubility of carbon dioxide and oxygen in the nutrient solution. With this differential type of manometer both oxygen and carbon dioxide changes can be measured.

Another method frequently employed, especially in ecological studies, is the determination of dissolved oxygen in closed vessels by titration (Winkler method). This method avoids the use of the somewhat non-physiological buffer mixture and is much simpler than the differential manometric method. However, it does not permit a series of measurements on a single sample.

Petering and Daniels (62) have recently applied the dropping-mercury electrode to a determination of dissolved oxygen changes in photosynthesis. As in the manometric method, repeated measurements may be made on a single sample of plant suspension. In at least two respects, this method is superior to the usual manometric method. It does not necessitate the use of buffer mixtures and it does not involve an equilibrium between gas and liquid phases. In speed of response it compares favorably with the spectrometric method of McAlister (53).

III. GENERAL DESCRIPTION OF THE PHOTOSYNTHETIC PROCESS

The equation for the reaction involved in photosynthesis in green plants is often written as follows:



This equation, when reversed, becomes the one usually used to represent the normal respiratory process.

It is usually assumed that formaldehyde is the first product of photosynthesis, and that subsequent polymerization is responsible for the formation of glucose or other carbohydrates. If formaldehyde is the first product, then ΔH for equation I becomes 134,000 cal. The subsequent polymerization reaction will then be exothermic. The necessary energy for photosynthesis is assumed to come from light absorbed by the two chlorophyll pigments in the plant, although it is possible that energy absorbed by other pigments, such as carotene and xanthophyll, may sometimes be utilized.³ It is rather remarkable that light of wave length as long as 7000 Å. (see figure 2), for which $Nh\nu$ is equal to 40,500 cal., will bring about a reaction for which ΔH is 112,000 cal. Evidently photosynthesis involves a more complex series of endothermic reactions than has been observed for any non-biological photoreaction.

Photosynthesis at different wave lengths

Figures 1 and 2 show a rather close correlation between relative rates of photosynthesis at different wave lengths (Hoover (42)) and the absorption spectra (in ether solution) of chlorophylls *a* and *b* (93). Hoover's results were obtained with young wheat plants, using equal incident light intensities (less than 300 foot-candles) at the various wave lengths. A wheat leaf contains enough chlorophyll to absorb a considerable fraction of the incident radiation, even in the region between 5000 and 6000 Å.; this accounts for the relatively high minimum in the photosynthesis curve (figure 2). Chlorophyll absorbs more strongly at 3660 Å. than in the region between 5000 and 6000 Å. (90). Consequently the low rate of

³ Except in the *Myxophyceae* (blue-green algae) the chlorophyll pigments are found only in restricted regions of the plant cell, known as chloroplasts. These regions also contain the yellow pigments carotene and xanthophyll. Frequently a large number of the cells in a green leaf contain no chloroplasts, while in the remaining cells the number may vary from one to many. Consequently only a small fraction of the total leaf volume consists of chloroplasts and hence is able to carry on photosynthesis. In many of the algae, however, the chloroplasts constitute a much larger fraction of the total plant material. For example, the single chloroplast in the unicellular green alga *Chlorella* probably occupies half of the cell volume.

This large proportion of photosynthetically active plant material constitutes one reason for the widespread use of *Chlorella* in photosynthesis investigations.

photosynthesis at 3660 Å. (figure 2) indicates a much lower quantum efficiency for the process than in the region from 4000 to 7000 Å. Below 3000 Å. ultraviolet radiation is distinctly injurious (57, 4).

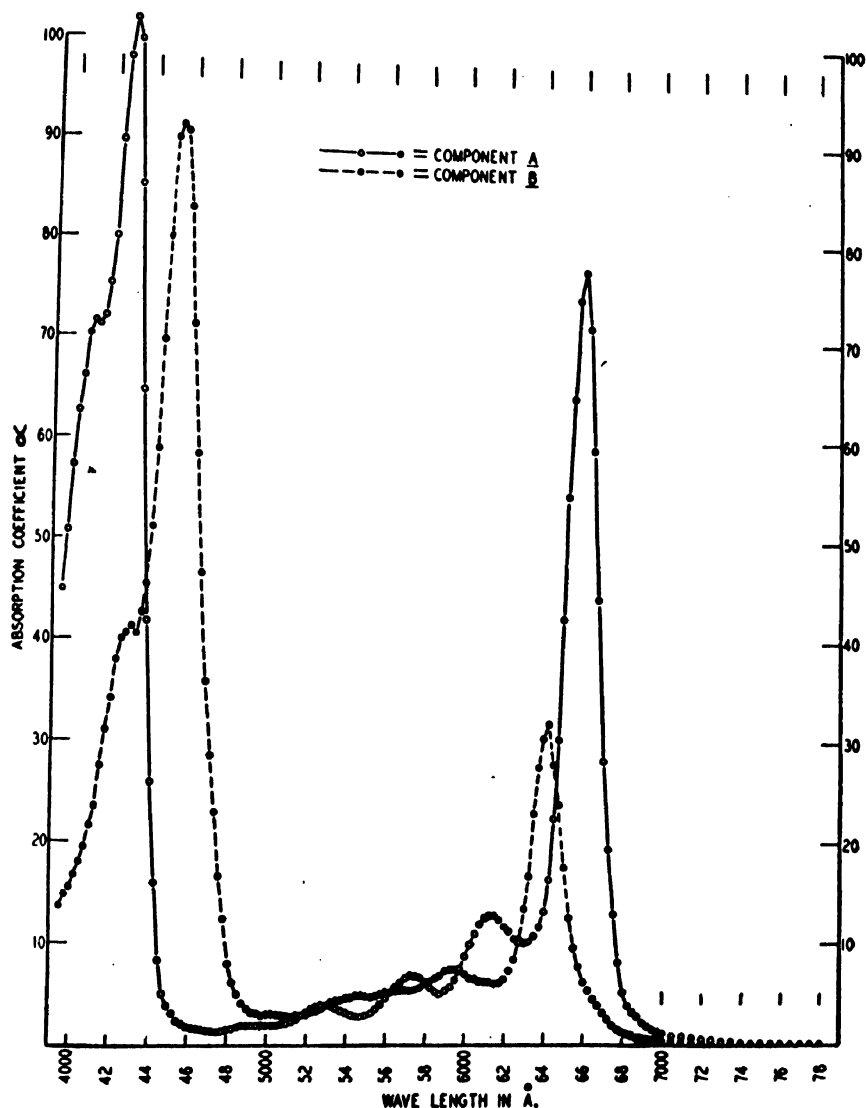


FIG. 1. The absorption spectra of chlorophylls *a* and *b* in ether (Zscheile (93))

The formaldehyde hypothesis

The occurrence of formaldehyde as an intermediate product of photosynthesis has been neither proved nor disproved (58). In any event its concentration must be very low, even during rapid photosynthesis, since

concentrations higher than a few hundredths of a per cent are distinctly toxic. The presence of small amounts of formaldehyde in green leaves has been reported by a number of investigators. Others have found that plants in the dark can utilize low concentrations of formaldehyde to form carbohydrates. These observations add plausibility to the hypothesis that formaldehyde is an intermediate product in the photosynthetic process, but do not constitute proof of the hypothesis, since formaldehyde

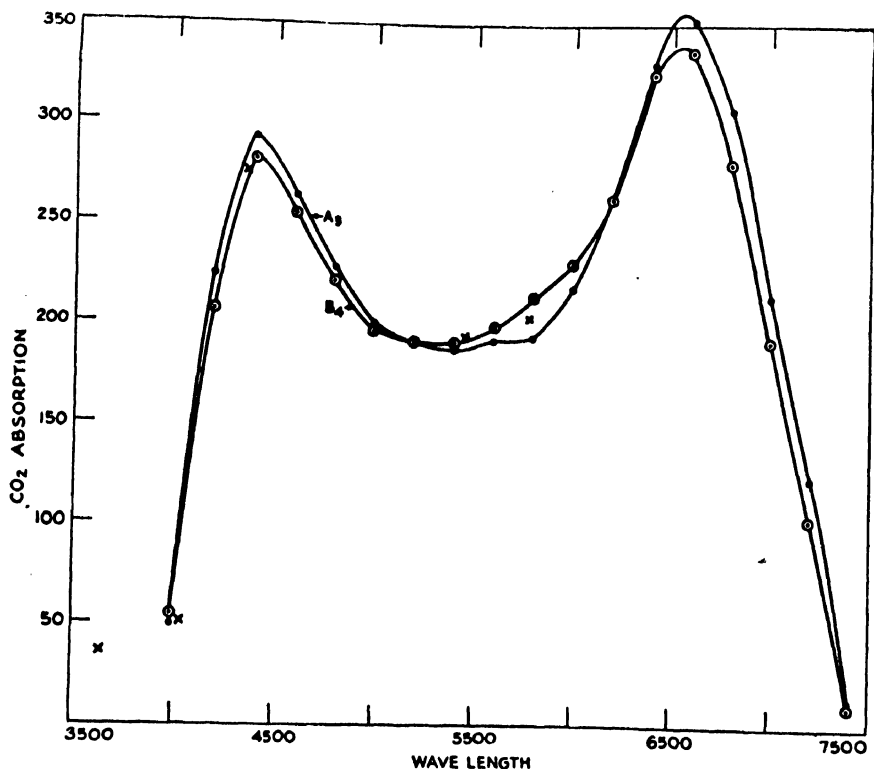


FIG. 2. Rate of photosynthesis as a function of wave length (low light intensity). A₁, the corrected form of the curve obtained with large Christianson filters; B₁, the corrected form of the curve obtained with small Christianson filters. Points marked X are the results obtained with line filters and quartz mercury arc. (Hoover (42)).

may be produced by other metabolic processes. Also, formaldehyde is only one of several organic compounds which may be utilized by plants in the formation of carbohydrates (58).

The photosynthetic quotient

The ratio of the number of moles of carbon dioxide absorbed to the number of moles of oxygen produced, $\Delta\text{CO}_2/\Delta\text{O}_2$, is called the photosyn-

thetic quotient.⁴ If glucose or some other carbohydrate is the final product of photosynthesis, the photosynthetic quotient should have a value of 1, as in equation I. Maquenne and Demoussy (56) and Willstätter and Stoll (89) investigated a large number of different plants and found a quotient very close to unity. Apparent values markedly different from unity are sometimes obtained, but these may often be attributed to the effects of abnormal respiration or other processes.

The value of the photosynthetic quotient constitutes the principal proof that a carbohydrate is the first product of photosynthesis. Many investigators have attempted to identify this carbohydrate product. From present evidence it may be considered probable that a hexose is the first product formed, though the prior formation of sucrose remains as a possibility.⁵

In diatoms (and also in some other plants) the products of photosynthesis are stored principally in the form of oils rather than as carbohydrates. Barker (10) has measured the photosynthetic quotient in two species of diatoms in an effort to determine whether the oils are formed as primary products of photosynthesis or whether they are secondary metabolic products. For complete conversion of the carbon dioxide to oils, the quotient should be approximately 0.70 instead of 1.00. For both species of diatoms Barker found a quotient close to 0.95, with a tendency for the value to increase slightly with increasing light intensity. He concluded that 10 per cent or less of the photosynthetic products appeared as stored fat and that this fat production was probably the result of a secondary reaction.⁶

The effect of light intensity and temperature on the rate of photosynthesis

Figure 3 shows diagrammatically the relation between the rate of photosynthesis and light intensity at high carbon dioxide concentration. Curve A represents the behavior at a relatively low temperature, perhaps 10°C.; curve B is for a higher temperature, such as 20°C.

While the type of behavior shown in figure 3 is characteristic of most

⁴ Some writers apply the term "photosynthetic quotient" to the reciprocal of this ratio, i.e., $\Delta\text{O}_2/\Delta\text{CO}_2$.

⁵ More complete discussions of this problem are given by Spoehr (reference 70, page 215) and Stiles (reference 74, page 151).

⁶ When a simple alga, such as *Chlorella*, is grown under long-continued constant conditions, including constant illumination, it is probable that an equilibrium is reached between the rate (per unit of plant material) at which food is manufactured by photosynthesis and the rate at which it is used in growth. Under these conditions the *apparent* photosynthetic quotient (i.e., uncorrected for respiration) should give a measure of the average state of oxidation of the entire cell material. The oxygen eliminated during the reduction of nitrates to protein material should contribute noticeably to a lowering of the apparent quotient.

plants which have been studied, the exact numerical behavior may vary widely. Thus, in many land plants the maximum photosynthetic rate may not be reached until the light intensity approaches that of sunlight, while in other plants, particularly some of the algae, one-tenth of this intensity may produce the maximum rate.⁷

The shape of a rate-light intensity curve will depend on the fraction of light absorbed by the plant material under investigation. With a thick leaf containing an abundance of mesophyll, or with a dense suspension of algae, different portions of the plant material will be exposed to widely

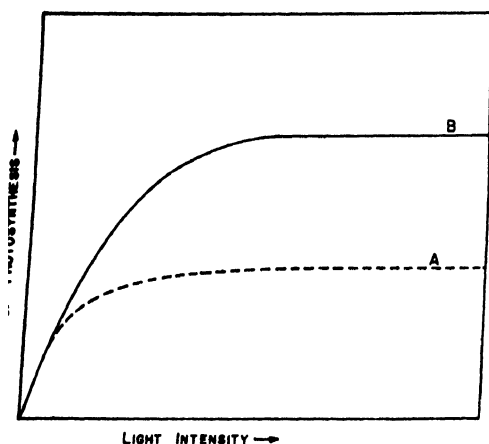


FIG. 3

FIG. 3. Rate of photosynthesis as a function of light intensity. A, low temperature curve; B, high temperature curve.

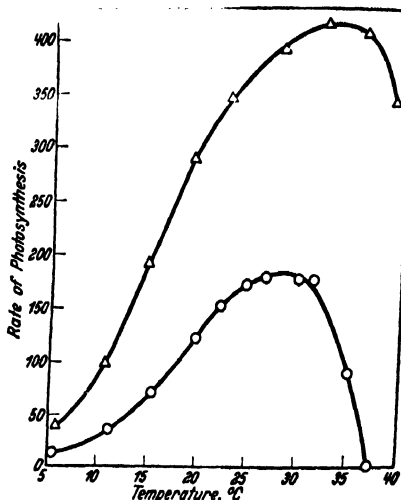


FIG. 4

FIG. 4. Variation in rate of photosynthesis with temperature at high light intensities for *Nitzschia closterium* (O) and *Nitzschia palea* (Δ). Photosynthesis is expressed in cubic millimeters of evolved oxygen per hour per 10 cmm. of cells. (Barker (10)).

different light intensities. A very high incident intensity will then be necessary to produce a maximum photosynthetic rate in the chloroplasts farthest removed from the incident surface.

As shown in figure 3, the rate of photosynthesis is nearly independent of temperature at low light intensities, but becomes temperature-dependent at higher intensities. Thus, for *Chlorella* Warburg (82) found a temperature coefficient (Q_{10}) of unity at approximately 6×10^3 ergs per

⁷ In some plants the rate of photosynthesis may increase to a maximum and then decrease again as the light intensity is increased (48, 54, 72). The reason for a decrease in rate at high intensities is not definitely known. It may be caused by some form of injury, or it may be caused by the simultaneous occurrence of photooxidation processes.

cm.² per second,⁸ but a coefficient of from 2 to 5 (depending upon the temperature) at an intensity of approximately 100×10^8 ergs per cm.² per second.

From the type of behavior shown in figure 3, as well as from other evidence to be discussed below, it must be concluded that photosynthesis is a complex cyclic reaction, involving at least one thermal reaction, usually known as the Blackman reaction,⁹ in addition to whatever photoreactions are necessary. According to this view, at low light intensities, where the rate of photosynthesis is approximately proportional to the intensity, the time between the absorption of successive photons, by that portion of the mechanism involved in the reduction of a single carbon dioxide molecule, will be sufficient to permit the Blackman reaction to be completed. Light is then said to be the limiting factor. But at high intensities, where the rate has practically reached its maximum value (so-called light saturation), the rate will presumably be limited only by the rate of the Blackman reaction.¹⁰ This implies that photons are absorbed so rapidly by the mechanism that the average time between the completion of the Blackman reaction and the next light absorption will be very short compared with the average time required for the Blackman reaction. An increase in temperature will increase the rate of the Blackman reaction without appreciably altering the rate of the light reaction.¹¹

⁸ In this research Warburg made only approximate estimates of absolute intensities.

⁹ The term "Blackman reaction" as used in this paper refers to any reaction or reactions which contribute to the temperature dependence of the photosynthetic process. It is named for F. F. Blackman, who, in 1905 (12), formulated his principle of limiting factors in the following words: "When a process is conditioned as to its rapidity by a number of separate factors, the rate of the process is limited by the pace of the 'slowest' factor." Application of this principle did much to clarify the contradictory results of earlier research on photosynthesis.

Many subsequent investigators appear to have interpreted this principle too literally, i.e., they have assumed that for measurements under ideal conditions only a single factor could influence the rate of photosynthesis at any one time. According to this view, an increase in the intensity of a particular variable should result in an abrupt transition from direct dependence of the rate on this variable to complete independence. Such a transition is contrary to any reasonable kinetic formulation of the process.

¹⁰ According to a recent mechanism of Franck and Herzfeld (34), the rate of the Blackman reaction is not limiting at high light intensity (see page 850).

¹¹ Warburg and Uyesugi (87) and Yabusoe (92) found some similarities between the Blackman reaction and the rate of decomposition of hydrogen peroxide by the enzyme catalase. There has therefore been a widespread belief that the Blackman reaction consists of a reaction between catalase and a peroxide. Hence many postulated mechanisms have included hydrogen peroxide or organic peroxides as intermediate products in photosynthesis. However, Emerson and Green (28) have recently made further comparisons of the two reactions without finding any significant similarity.

Figures 4 and 5 illustrate the effect of temperature on the rate of photosynthesis at high light intensity and high carbon dioxide concentration. Figure 4 gives the results obtained by Barker (10) with two species of diatoms; figure 5 gives the results obtained by Craig and Trelease (21) with *Chlorella vulgaris*. The lower curves in figure 5 are for rate measurements in 99.9 per cent heavy water. (The heavy water experiments will be discussed below, page 828.) The decrease in photosynthetic rate at high temperatures is probably due to injury to the plant material. Further evidence of injury is found in the fact that the photosynthetic rate at high temperatures is not constant, but decreases with time. Injury may be due to deactivation of enzymes (or of an enzyme-producing mechanism) connected with the Blackman reaction, or it may be due to a change in the physical condition of the chloroplasts.

The Arrhenius equation may be used to calculate apparent activation energies for the temperature-sensitive reaction in photosynthesis. How-

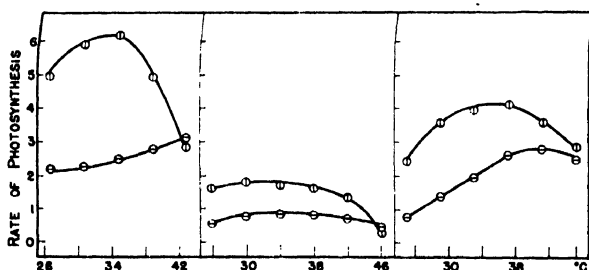


FIG. 5. Rate of photosynthesis as a function of temperature. For H_2O shown by circles with vertical bars, and for D_2O shown by circles with horizontal bars. (Craig and Trelease (21)).

ever, in view of the complex system involved, the significance of the figures so obtained is doubtful. The apparent activation energy varies for different species and decreases with increasing temperature. The low temperature value for *Chlorella pyrenoidosa* and *Hormidium flaccidum* has been reported as being approximately 20,000 cal. (27, 78). Barker (10) found a value of about 30,000 cal. for the diatoms *Nitzschia closterium* and *Nitzschia palea* (see figure 4). Emerson and Green (27) found a value of approximately 50,000 cal. for *Chlorella vulgaris* and for the marine alga *Gigartina harveyana*.

The effect of carbon dioxide concentration on the rate of photosynthesis

Variation in carbon dioxide concentration apparently affects the rate of photosynthesis in a manner similar to variation in light intensity. Van den Honert (reference 77, page 225), working with moist films of *Hormid-*

ium at 12° and 20°C., and using high light intensity, obtained curves essentially like those of figure 3 (with light intensity replaced by carbon dioxide concentration). In both curves the rate of photosynthesis reached its maximum value at a carbon dioxide concentration of about 0.04 per cent by volume. (Normal carbon dioxide concentration in air is approximately 0.03 per cent.) For young wheat plants Hoover, Johnston, and Frackett (43) found that a higher carbon dioxide concentration, approximately 0.15 per cent, was necessary for a maximum rate of photosynthesis (light intensity one-fourth of that of sunlight). Light saturation was not reached in this work; at higher light intensities still higher carbon dioxide concentrations would have been required. In general, the diffusion of carbon dioxide into a chloroplast will encounter more resistance in a leaf, where most of the chloroplast-containing cells are usually some distance from the leaf surface, than in a small unicellular or filamentous alga, where every vegetative cell is photosynthetically active and not surrounded by other cells. A higher carbon dioxide concentration will then be necessary for leaves in order to overcome this diffusion resistance.¹²

For *Chlorella* in liquid suspension Emerson and Green (29) found that a carbon dioxide concentration of 10 or 15 $\times 10^{-6}$ moles per liter was sufficient for maximum photosynthesis.

Smith (68), using the water plant *Cabomba*, has studied the effect of light intensity and carbon dioxide concentration on the photosynthetic rate. He found that both variables affected the rate in the same way.

However, there is disagreement concerning the effect of temperature at low carbon dioxide concentrations. According to van den Honert's curves (reference 77, page 225), temperature is without effect on the rate at low concentrations, but Warburg (82) and Emerson (23) found a high temperature coefficient for *Chlorella* at low carbon dioxide concentrations. Both Warburg and Emerson used the manometric method in their measurements; the *Chlorella* was suspended in carbonate-bicarbonate buffer mixtures and the concentration of free carbon dioxide was varied by varying the ratio of carbonate to bicarbonate. At least three possible objections may be raised to the use of these buffers for regulating carbon dioxide concentration: (1) In varying the carbon dioxide concentration, the pH is also varied. The high pH necessary to obtain limiting carbon dioxide concentrations may influence the photosynthetic rate. (2) A high concentration of carbonate or bicarbonate ions may inhibit photosynthesis. (3) It is possible that water plants may be able to use carbonate or bicarbonate in the photosynthetic process (3). Emerson and Green (29), working with phosphate buffers, found that within the range from pH 4.6 to 8.9, neither bicarbonate nor hydrogen ion influenced the rate of photo-

¹²The problem of diffusion resistance has been discussed by James (47).

synthesis at saturating concentrations of carbon dioxide. They concluded, however, that in carbonate mixtures at a higher pH, other factors, probably carbonate and bicarbonate concentrations as well as free carbon dioxide concentration, were influencing the rate of photosynthesis. Moreover, with the phosphate buffers, their measurements of photosynthesis in *Chlorella* as a function of carbon dioxide concentration more closely resembled van den Honert's results for *Hormidium* than Warburg's results for *Chlorella* in carbonate-bicarbonate buffers. On the basis of the results of Emerson and Green, it may be considered probable that van den Honert's curves (77), showing little or no temperature effect at low carbon dioxide concentration, are valid for *Chlorella* as well as for *Hormidium*.

Since a knowledge of the temperature effect at low carbon dioxide concentrations is of importance in choosing a mechanism for the photosynthetic process (see page 841), it appears desirable that a further study should be made of this effect in both algae and higher plants.

The influence of intermittent light on photosynthesis

Warburg (82), Emerson and Arnold (25), and Pratt and Trelease (64) have studied the effect of intermittent light on photosynthesis in *Chlorella*.

Warburg used a rotating sector which cut out half of the incident light. He found that at high light intensity and abundant carbon dioxide concentration a given amount of light produced more photosynthesis when absorbed intermittently by the *Chlorella* than when it was absorbed continuously. Moreover, the improvement in yield depended upon the frequency of the flashing. At low light intensities, intermittent light produced no improvement in yield.

The effect of intermittent light can be explained on the basis of the cyclic mechanism discussed above (page 823). Thus, after a sufficiently long period of intense illumination, most of the chlorophyll molecules would be activated (or combined in an unstable compound) and waiting to undergo the so-called Blackman reaction. Photons absorbed by these molecules would presumably be without effect on the photosynthetic rate. But, if this period of intense illumination were followed by a sufficiently long period of darkness, the Blackman or thermal reaction should continue until completed. Then, at the beginning of the next light flash, all of the photons would presumably be absorbed by chlorophyll molecules ready to undergo the next photosynthetic cycle. By combining very short light flashes with long dark periods it should be possible, according to this picture, to have a plant utilize intermittent light of high intensity as efficiently as it can utilize continuous light of low intensity.

Emerson and Arnold (25) have extended considerably the observations of Warburg. They used a neon tube as a light source, with an electrical circuit which gave very short light flashes. The circuit was constructed

so that the length of the dark periods could be varied without appreciable effect on the light flashes. The *Chlorella* was suspended in a buffer mixture and photosynthesis was measured manometrically.

Figure 6 shows the results obtained by Emerson and Arnold in their study of the effect of dark time on the yield of photosynthesis per flash. The lower curve was obtained at 1.1°C., while the two upper series were obtained at 25°C. All of the measurements shown in figure 6 were made with *Chlorella* cells from the same culture. It appears that at 25°C. a dark period of 0.04 sec. is sufficient for practical completion of the thermal

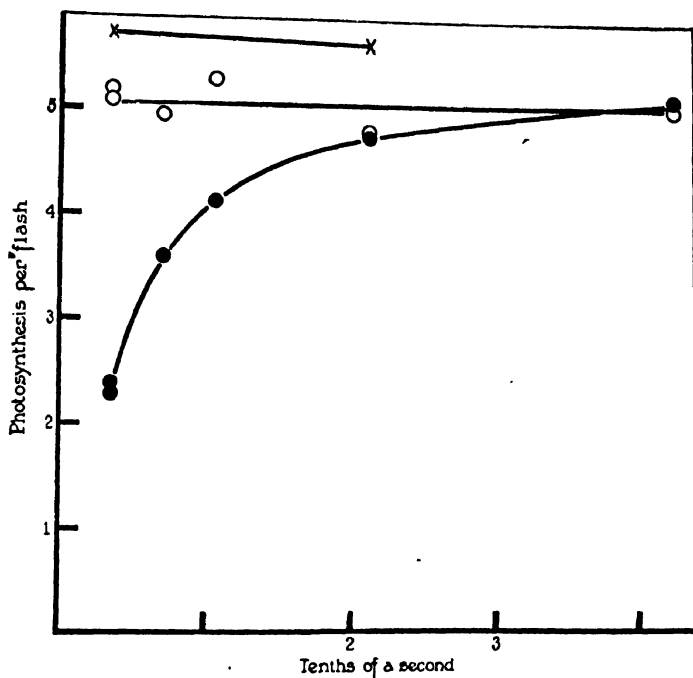


FIG. 6. The effect of dark time on the yield of photosynthesis per flash of light. Open circles are points made at 25°C.; solid circles at 1.1°C. The crosses are a check made at 25°C. (Emerson and Arnold (25)).

or Blackman reaction, while at 1.1°C. a period of 0.2 or 0.3 sec. is required for practical completion. In these experiments of Emerson and Arnold, the duration of each light flash was less than 2×10^{-5} sec., a period which is short compared with the average duration of the thermal reaction, at least at 1.1°C.

Figure 7 shows the results obtained with *Chlorella* at high light intensity and at 23.9°C. by Pratt and Trelease (64). Using *Chlorella* cells suspended in heavy water as well as in ordinary water, they studied the effect of flashing light on the rate of photosynthesis. Each light flash in these

experiments lasted about 0.0045 sec. This period was much longer than that used by Emerson and Arnold. Consequently a considerable fraction of the chlorophyll molecules probably went through the reaction cycle more than once for each flash.

The point corresponding to a dark period of 0.0122 sec. on the upper curve in figure 7 is apparently slightly lower than the maximum, suggesting that the Blackman reaction is not quite completed in 0.01 sec. at 24°C. This is in approximate accord with indirect calculations of Emerson and Arnold (26) which indicated an *average* time of 0.012 sec. for the completion of a cycle (photochemical + Blackman reactions) in *Chlorella* at 25°C.

The lower curve in figure 7 was obtained from experiments in which the algae were suspended in heavy water. Evidently deuterium oxide retards the Blackman reaction without appreciably affecting the photochemical reaction, since, with a long dark period, the amount of photosynthesis per flash is the same in heavy water as in ordinary water.¹³ These observa-

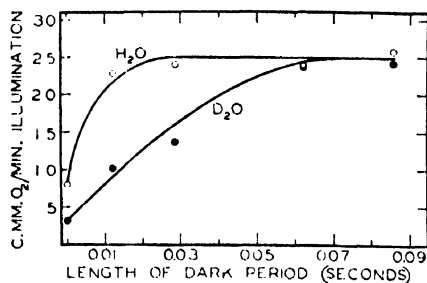


FIG. 7. Rate of photosynthesis in *Chlorella vulgaris* per minute of actual illumination as a function of the length of the dark period. The values are proportional to the photosynthesis per flash. (Pratt and Trelease (64)).

tions indicate that the specific effect of deuterium oxide is manifested in the Blackman reaction. Possibly the replacement of water by deuterium oxide may reduce the rate of the Blackman reaction by affecting a specific enzyme system.

Emerson and Arnold (25) have studied the effect of low concentrations of hydrogen cyanide on photosynthesis in *Chlorella* in flashing light. With a hydrogen cyanide concentration of 1.14×10^{-4} moles per liter, the effect was very similar to that of 99.9 per cent deuterium oxide, as reported by

¹³ With continuous light of high intensity, according to the measurements of Craig and Trelease (21), the rate of photosynthesis in D₂O is about 40 per cent of the rate in H₂O, except at very high temperatures (see figure 5), where the rate in H₂O falls more rapidly than the rate in D₂O. At low light intensities the rates in D₂O and H₂O become nearly equal. These observations are in agreement with the conclusions indicated by the flashing light experiments.

Pratt and Trelease (64) (see figure 7). The Blackman reaction was retarded but the maximum yield per flash was unchanged. But, if the hydrogen cyanide was replaced by a low concentration of phenylurethan or thymol, the maximum yield of photosynthesis per flash was decreased, with only a slight retardation of the Blackman reaction.¹⁴

Figure 8 shows the observations of Emerson and Arnold concerning the influence of carbon dioxide concentration on the yield of photosynthesis per flash. As before, the flash duration was less than 2×10^{-8} sec. They concluded from these experiments that carbon dioxide enters the process

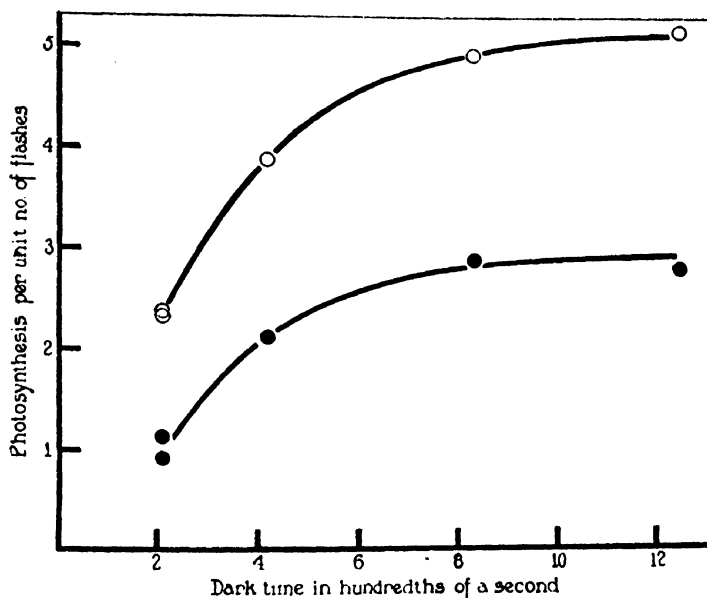


FIG. 8. The course of the dark reaction at two different concentrations of carbon dioxide. Open circles, carbon dioxide concentration = 71×10^{-6} moles per liter; solid circles, carbon dioxide concentration = 4.1×10^{-6} moles per liter. (Emerson and Arnold (25)).

of photosynthesis either before or (less likely) coincident with the photochemical reaction. If chlorophyll alone were involved in the light reaction, then, according to their argument, a lower carbon dioxide concentration would not decrease the yield per flash but would necessitate longer dark periods for full utilization of the light. Since the opposite effect was actually found, Emerson and Arnold concluded that both chlorophyll and carbon dioxide (perhaps in combination) are required for the light reaction.

¹⁴ In continuous light, narcotics such as phenylurethan and thymol inhibit photosynthesis at both high and low light intensities, in contrast to hydrogen cyanide, which inhibits only at high intensities (83).

However, it appears that this conclusion is open to question from two points of view. In the first place, carbon dioxide concentration was varied by changing the proportion of carbonate to bicarbonate in the buffer mixtures. Later experiments of Emerson and Green (29) have thrown doubt on the validity of this method of obtaining low carbon dioxide concentrations (see page 825). Secondly, it appears that the argument of Emerson and Arnold (given in the preceding paragraph) would be strictly valid only if the average lifetime of an activated chlorophyll molecule were much longer than the average time required for the Blackman reaction. Otherwise, the lower curve in figure 8 could be interpreted as the resultant of two curves, one a slowly rising curve, like the lower curve in figure 7, and the other a falling curve representing a decrease in concentration of activated chlorophyll.

Although the behavior illustrated in figure 8 may not give very definite evidence concerning the order in which certain steps in the reaction cycle may occur, it probably indicates, as Emerson has pointed out (reference 23, page 319), that carbon dioxide enters into a reaction in the photosynthetic cycle other than the Blackman reaction, since, if the latter reaction alone were affected by carbon dioxide concentration, the maximum yield of photosynthesis per flash should remain constant. However, this last conclusion is still subject to the uncertainty concerning the influence of carbonate-bicarbonate buffers.

Other experiments involving the use of intermittent light will be discussed below (see pages 831 and 845).

The induction period in photosynthesis

A number of investigators have observed an induction period in photosynthesis, but the characteristics of this period appear to vary widely in different plant species. In the marine alga *Ulva*, Osterhout and Haas (61) found that about 2 hr. were necessary for attainment of a steady rate at high light intensity. In the moss *Mnium*, Briggs (14) found an induction period of nearly an hour. Emerson and Green (27) found a period of about 20 min. for the marine alga *Gigartina*. A period of 3 min. or less has been found in *Chlorella* (83), *Hormidium* (78), *Cabomba* (69), and wheat (53). After a 10-hr. period of darkness, however, McAlister found a longer induction period for wheat, about 12 min. Warburg found an induction period in *Chlorella* only at high light intensities, but for *Cabomba*, Smith observed an induction period at both high and low intensities. However, Warburg's measurements extended to lower intensity values than did those of Smith.

This wide diversity of characteristics suggests that the induction period may be caused by different mechanisms in different plants. Smith (69) has derived an equation for the induction period, relating the relative rate

of photosynthesis to the duration of illumination, which satisfactorily describes his own data and also data obtained by several other investigators. However, the application of this equation to a particular series of data depends upon the evaluation of a constant which determines the time scale.

Most methods for measuring photosynthesis have too great a time lag to permit a satisfactory direct study of an induction period as short as 3 min. Warburg, van der Paauw, and Smith measured photosynthesis manometrically in their experiments, and resorted to an indirect integration method for studying the short induction periods which they encountered. Smith, for example, determined respiration for a 30-min. period and then exposed the plant (*Cabomba*) to light for 1 min. The manometer was not read until after a further 5- or 10-min. dark period. The rate so determined was, in effect, the resultant of 1 min. of photosynthesis superimposed on a 6- or 11-min. period of respiration. The procedure was then repeated for the same or for successively longer light exposures. The methods of Warburg and van der Paauw were similar to this. A potential source of error in this type of procedure is the possible stimulation of respiration by light. With a short light period such as 1 min., even a slight increase in respiratory rate during the subsequent 5- or 10-min. dark period would greatly reduce the apparent yield of photosynthesis.

Because of the very small time lag in his apparatus (see page 816), McAlister (53) was able to determine the induction period in wheat from continuous measurements of the photosynthetic rate. Considering the amount of carbon dioxide lost to photosynthesis as a measure of the induction period, he found that, in wheat, this quantity decreased with decreasing light intensity, apparently approaching zero at zero intensity. This result is in qualitative agreement with the behavior in *Chlorella* (83) and in *Cabomba* (69). McAlister also found the induction period in wheat to be nearly twice as long at 12°C. as at 31°C. Van der Paauw (78) observed a similar temperature effect in *Hormidium*.

In intermittent light, with equal light and dark periods, the rate of photosynthesis in wheat passes through a minimum for light and dark periods of about 1 min. (53). With longer intervals a smaller percentage of total illumination time is taken up by the induction periods, while at shorter intervals it is probable that two factors contribute to an increase in rate. One is the occurrence of the Blackman reaction during the dark periods (see page 826); the other is the probability that, after a short dark interval, the induction period is less pronounced than after a longer interval.

No very convincing mechanism has so far been advanced for the induction process in photosynthesis. Since three or more quanta of red light are necessary to supply energy for the reduction of one molecule of carbon

dioxide to carbohydrate, it is often assumed that the process occurs through a series of three or more intermediate photochemical reactions (however, see page 851). On this basis it would appear probable that, after a long dark period, each reaction unit in the chloroplast would have to undergo some or all of this series of reactions before evolving oxygen or absorbing additional carbon dioxide. This should produce an induction period lasting until the establishment of equilibrium between the concentration of the various intermediates. Furthermore, the magnitude of the induction effect after a dark interval should give a measure of the extent to which the various intermediate compounds were decomposed during the dark interval.

According to this picture the induction period should last much longer at low light intensities than at high intensities. This is contrary to the observed facts. Consequently, it is evident that processes other than those considered in the preceding paragraph must play a part in the induction period.

According to the mechanism of Franck and Herzfeld (34), oxygen is evolved after the first photochemical step in the series of reduction reactions. They suggested that the induction period is the result of photo-oxidation processes (see page 850).

It appears that further data concerning the influence on the induction period of various external and internal factors are greatly to be desired.

Quantum efficiency of photosynthesis

A knowledge of the quantum efficiency of the photochemical process in photosynthesis is essential to any detailed consideration of the kinetics of the process. Unfortunately, the actual measurement of this quantity is accompanied by difficulties not encountered in quantum efficiency measurements carried out in non-living systems. Some of these difficulties will be considered in the following paragraphs.

Because of the complexity of the photosynthetic process, many factors other than the efficiency of the photoprocess may influence quantum efficiency values determined from a measurement of the overall reaction. To a certain extent, the influence of these other factors may be minimized by using low light intensities, high carbon dioxide concentration, and a relatively high temperature. In this range, since the rate of photosynthesis is nearly proportional to light intensity, the quantum efficiency should be nearly constant and relatively independent of other external variables. Under these conditions, however, the necessary correction for respiration becomes relatively very large. If it were definitely established that the respiratory and photosynthetic processes are independent and unaffected by each other, and that the rate of respiration is not influenced by light, then respiration corrections, even when large, would not seriously

reduce the accuracy of photosynthesis measurements. However, van der Paauw (78) found that, in *Hormidium*, respiration was more than twice as rapid immediately after an hour of strong illumination as it had been before the photosynthetic period. Two hours after exposure, the respiration had dropped to its normal rate. In an atmosphere devoid of carbon dioxide, van der Paauw found that the respiratory rate was actually increased during illumination. However, it is possible that, in the absence of carbon dioxide, light may have produced an abnormal effect. Petering and Daniels (62) have observed a temporary increase in the rate of respiration for *Chlorella* after exposure to light, the extent of the increase depending on the previous treatment. On the other hand, McAlister (53) failed to find any stimulation in wheat plants after illumination at high light intensities, despite the fact that a very sensitive method was used. The difference between the response of wheat on the one hand, and *Hormidium* and *Chlorella* on the other, may be partially due to the much larger fraction of total cell volume occupied by the chloroplasts in the case of the algae.

The measurement of light absorption in plant material is difficult. Pigments are irregularly distributed and much light is lost by refraction and scattering. From this point of view, a small unicellular alga, such as *Chlorella*, is more satisfactory than a leaf of a higher plant. *Chlorella* in suspension settles only slowly, making it easy to maintain even distribution. Moreover, by varying the concentration of the suspension, the fraction of incident light absorbed can be varied at will.

Not all of the absorbed light is absorbed by chlorophyll. The amount absorbed by other substances can be estimated from measurements made with extracted pigments, but such an estimate is uncertain, since the optical properties and distribution of the various pigments are altered by the extraction process. Moreover, it is not known whether light absorbed by chloroplast pigments other than chlorophyll can contribute to photosynthesis. At wave lengths longer than 5500 Å., the uncertainty due to these other pigments is minimized, since their absorption is very slight at longer wave lengths.

Another difficulty is found in the fact that, in some plant material, a large part of the chlorophyll may be inactive so far as ability to produce photosynthesis is concerned. After reaching maturity a leaf usually decreases in photosynthetic activity, even though the amount of chlorophyll may remain constant or increase. Because of this, it is advisable to use only young or actively growing material for quantum efficiency measurements:

Finally, there is a possibility that the mechanism of photosynthesis is not the same for all plants. In this case the overall efficiency would probably vary in different plants, even if all measurements were made under

ideal conditions. However, the apparently identical nature of the pigments in many different plant species, as well as other similarities in the photosynthetic process, suggest that the photochemical reactions are the same, at least throughout the green algae (*Chlorophyceae*) and the higher divisions of the plant kingdom (mosses, ferns, and seed plants).

The first measurements of the quantum efficiency of photosynthesis were made by Warburg and Negelein (85, 86), with the alga *Chlorella* as plant material. A differential manometer was used for the photosynthesis measurements. A mercury arc with filters served as a source of monochromatic light except in the red, where a filament lamp with filters was used to obtain the region 6100–6900 Å. To avoid the necessity of measuring transmitted light, Warburg and Negelein used very heavy suspensions of the algae. Except for a small amount of reflection, practically all of the incident light was absorbed. At any one time most of the *Chlorella* cells were thus receiving only a small fraction of the incident light intensity. To reduce the value of the respiration correction, these investigators carried out their measurements at a temperature of 10°C., where respiration is much slower than at 20° or 25°C.

At wave lengths of 6600, 5780, and 5461 Å. Warburg and Negelein found a quantum efficiency of approximately 0.25 molecule of carbon dioxide per quantum. The observed value at 4360 Å. was lower, about 0.20, but an approximate correction for light absorbed by the carotene and xanthophyll pigments increased the 4360 Å. value to 0.25 or slightly higher. The incident light intensity in these experiments varied from 575 to 3500 ergs per cm.² per second. Within this range the quantum efficiency appeared to be independent of light intensity.

At 6600 Å. $Nh\nu = 43,000$ cal., so that a quantum efficiency of 0.25 corresponds to an energy efficiency of 65 per cent on the basis of equation I. If formaldehyde is the first product of photosynthesis, then ΔH for equation I becomes 134,000 cal. and the corresponding energy efficiency is 78 per cent. In either case the energy efficiency is surprisingly large, particularly since one or more of the intermediate reactions in photosynthesis is probably exothermic.

The quantum efficiency of photosynthesis in *Chlorella* has recently been investigated by Manning, Stauffer, Duggar, and Daniels (55). These investigators found quantum efficiencies much lower than those reported by Warburg and Negelein. Most of the experiments were carried out at 25°C., with high carbon dioxide concentrations. Light intensities varied from 830 to 24,000 ergs per cm.² per second. A mercury arc was used with a monochromator to give monochromatic light of wave lengths 5461 and 4360 Å. Other measurements were made with polychromatic light from the mercury arc, and still others with light from a tungsten filament lamp.

In some experiments a gas stream was bubbled through the algal suspension and photosynthesis measured by gas analysis, while in other experiments a closed system was used, oxygen being determined by the Winkler method. In all cases the algal suspensions were less concentrated than those of Warburg and Negelein, since from 10 to 50 per cent of the incident light was transmitted through the back of the reaction vessel.

The quantum efficiency values obtained by Manning, Stauffer, Duggar, and Daniels were quite variable, but the maximum value of approximately 0.06 is so far below the figure obtained by Warburg and Negelein that it is difficult to attribute the discrepancy to differences in experimental procedure.¹⁵ Different strains of *Chlorella* (possibly different species) may have been used in the two investigations (reference 55, page 272), but it is unlikely that such minor differences would cause any fundamental difference in the photosynthetic mechanism.

Quantum efficiency measurements, in *Chlorella* exposed to various intensities of sunlight below the surface of a lake, have been made by Manning, Juday, and Wolf (54). The maximum value approached at low light intensities was approximately 0.05.

Burns (18) has calculated quantum efficiencies from measurements of photosynthesis in white pine trees. In his experiments the top of a young tree was enclosed in a bell jar containing 1 per cent of carbon dioxide. The decrease in carbon dioxide concentration after 2 hr. of illumination was determined by gas analysis. Light sources were the 5890 Å. line of sodium, the 5780 Å. line of mercury, and polychromatic light with filters. The quantum efficiency for the yellow lines of sodium and mercury was approximately 0.13; for the polychromatic light the value was approximately 0.11. The light intensities used were apparently greater than 10,000 ergs per cm.² per second.

In Burns' experiments it was necessary to estimate the amount of absorbed light by determining the absorption of an acetone solution of the extracted pigments. This procedure is subject to some uncertainty, since the pigment distribution is of course very different in the two cases. Such an approximation is apparently unavoidable when working with a light-absorbing system as complex as this.

¹⁵ In both investigations it was evident that the previous conditions of growth played an important part in determining quantum efficiency values. Warburg and Negelein found that a week of growth at high light intensity, followed by a week of growth at low light intensity, gave the most favorable results for their strain of *Chlorella*. It is especially necessary to avoid using old cultures which have passed the period of most active growth. *Chlorella* cells from such cultures often contain a high chlorophyll concentration, but nevertheless show a low photosynthetic efficiency. It is possible that much of the chlorophyll in such cells is unable to transfer absorbed energy to the photosynthetic mechanism.

Briggs (13) has determined the energy utilization for photosynthesis in the leaves of the bean (*Phaseolus vulgaris*), the elder (*Sambucus nigra*), and the elm. Most of the light intensities were in the neighborhood of 5000 ergs per cm.² per second. The higher quantum efficiencies estimated from Briggs' data are in approximate agreement with those determined by Burns.

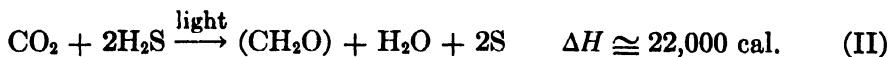
The present data concerning the problem of the quantum efficiency of photosynthesis are in serious disagreement. Evidently a further study of the problem is greatly to be desired. It appears probable that accurate and extensive data on the variation of the quantum efficiency as a function of wave length in different species may help to dispel the uncertainty concerning the photosynthetic activity of pigments other than chlorophyll, and also serve to provide a more secure basis for the postulation of chemical and kinetic mechanisms for the process.

Photosynthesis in bacteria

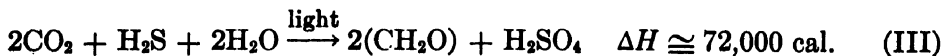
The problem of photosynthesis in bacteria is a very interesting one, and may have an important bearing on the problem of photosynthesis in green plants. An adequate discussion of bacterial photosynthesis would require many pages; only a few aspects of the problem will be considered here. More complete information may be obtained from recent publications of van Niel (79, 80), whose researches have contributed a large portion of our present knowledge concerning bacterial photosynthesis.

In the presence of light, hydrogen sulfide, and carbon dioxide, the green and purple sulfur bacteria are able to develop in entirely inorganic media. These bacteria grow only under anaerobic conditions, and no oxygen is given off during their development. Instead, sulfur or sulfuric acid is produced.

Assuming that formaldehyde is the first product, the equation for the process in the green sulfur bacteria may be written:

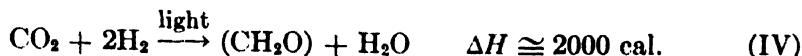


and in the purple bacteria:



Apparently the green sulfur bacteria can utilize only hydrogen sulfide as a hydrogen donor for the reduction of carbon dioxide, but the purple sulfur bacteria can carry on photosynthesis in the presence of a number of substances other than hydrogen sulfide. Among these are sodium sulfite, sodium thiosulfate, sulfur, hydrogen, and various organic substances

(79).¹⁶ For the reaction with hydrogen (37), the probable equation is

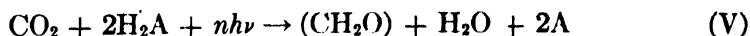


As Spoehr and Smith have pointed out (72), it is questionable whether the processes represented by equations II and IV can, strictly speaking, be called photosynthesis, at least if the word is used to denote an accumulation of light energy in the form of chemical energy. As in the higher plants, the formaldehyde or other intermediate product is presumably polymerized almost immediately to carbohydrates. If equations II and IV are written with glucose instead of formaldehyde as the reduction product, ΔH becomes approximately zero for equation II and negative for equation IV.

Bacterio-chlorophyll, a pigment closely related to the chlorophyll found in green plants (32), occurs in both of these groups of bacteria. The purple bacteria also contain one or more red pigments, probably related to the carotenoid pigments of green plants. Bacterio-chlorophyll shows a strong absorption in the region between 8000 and 9000 Å., in addition to its visible absorption bands. Consequently the sulfur bacteria are able to utilize infrared radiation in the reduction of carbon dioxide.

French (38) has studied the effect of different wave lengths on the rate of carbon dioxide assimilation by one of the purple bacteria (*Spirillum rubrum*). Using very thin suspensions of the bacteria, he found that the reaction rate corresponded closely to the absorption spectrum of the green pigment, even in regions where the red pigment absorbed strongly. Consequently he concluded that the red pigment is photochemically inactive in photosynthesis.

Van Niel has suggested that the various equations for photosynthesis (I to IV) should be considered as special cases of a general type reaction:



where H_2A represents a substance able to furnish hydrogen for the reduction of carbon dioxide.

Quantum efficiency of photosynthesis in bacteria

Roelefsen (66) has made some measurements of the quantum efficiency of photosynthesis in the purple sulfur bacteria. After making corrections for light absorbed by red pigments, he concluded that the maximum quantum efficiency is approximately 0.25 molecule of carbon dioxide per

¹⁶ The purple bacteria referred to here are members of the *Thiorhodaceae*. Another group of photosynthetically active purple bacteria, the *Athiorhodaceae*, apparently require organic compounds instead of sulfur compounds as reducing agents.

quantum absorbed, in agreement with the measurements of Warburg and Negelein (86) for the alga *Chlorella*.

French (37), using the purple bacterium *Streptococcus varians*, has made quantum efficiency measurements in which infrared radiation (wave lengths $8520 + 8940 \text{ \AA.}$, from a cesium lamp) was used as the energy source. The red pigments do not absorb appreciably in this wave length region. The bacterial suspension was in equilibrium with an atmosphere of 5 per cent carbon dioxide and 95 per cent hydrogen. Consequently the overall reaction presumably corresponded to that of equation IV.

French's measurements were complicated by the fact that he found a sigmoid curve for the variation in reaction rate as a function of light intensity. Thus, at low intensities the rate was proportional to a higher power of intensity than the first power. Quantum efficiencies were calculated from the maximum slopes observed for his rate versus light intensity curves. The maximum slope occurred at various light intensities, depending upon the type of pretreatment of the bacteria. By extrapolation French found that as the position of the maximum slope approached zero light intensity, the quantum efficiency appeared to approach a value of 0.25 (or 0.5 on the basis of hydrogen), in agreement with the estimates of Roelofson. As Emerson has pointed out (24), there is some doubt concerning the validity of this indirect method of calculating quantum efficiencies, particularly since it yields higher efficiency values than those actually prevailing in French's experiments.

French agrees with van Niel (79) in believing that the agreement between the quantum efficiencies observed for purple bacteria and those observed for *Chlorella* by Warburg and Negelein (86) indicate that a similar sequence of photoreactions is involved, despite the great difference in energy requirements. However, recent experiments with *Chlorella* (54, 55) have created some doubt concerning the correctness of the quantum efficiency values obtained by Warburg and Negelein (see page 835).

IV. THE RÔLE OF CHLOROPHYLL IN THE PHOTOSYNTHETIC PROCESS

Chlorophyll production

The manner in which chlorophyll is manufactured by green plants is a problem of fundamental physiological importance. It will be mentioned only briefly in this review, since it probably is not a direct part of the problem of photosynthesis. Further information on chlorophyll production may be obtained from articles by Spoehr and Smith (72), Inman, Rothmund, and Kettering (46), and Rothmund (67).

In most of the higher plants light is necessary for chlorophyll production. However, other plants, particularly some of the algae, can apparently produce chlorophyll in the dark. Etiolated plants, although usually

containing no chlorophyll, have been found to contain a very small amount of another green pigment which is usually called protochlorophyll. It differs spectroscopically from chlorophyll. When an etiolated plant is exposed to light, most of this green pigment disappears and is perhaps transformed into chlorophyll (67).

Most plants develop a higher chlorophyll concentration when grown in light of relatively low intensity than when grown in very bright light. Consequently several investigators have suggested that, in addition to its rôle in chlorophyll formation, light may also produce chlorophyll decomposition. According to this view, the chlorophyll concentration in a plant under given conditions can be regarded as a steady state concentration, with the rate of chlorophyll formation being approximately balanced by its rate of decomposition.

The production of chlorophyll is, of course, also dependent upon the proper supply of mineral nutrients; perhaps the most conspicuous of these are magnesium, which enters into the chlorophyll molecule, and iron, which apparently acts as a catalyst in some step in the formation process.

Chemical properties of chlorophyll

The structure and chemical properties of extracted chlorophyll are now known rather completely, largely as a result of the investigations of Willstätter, Stoll, Fischer, and Conant. The subject has recently been reviewed by Fischer (30) and by Steele (73). Figure 9 shows the probable formula for chlorophyll *a* (30). Fischer's formula for chlorophyll *b* is identical with the formula for *a*, except that the methyl group in the 3-position is replaced by a formyl group.

Willstätter and Stoll (89) have found that the *a:b* ratio for chlorophyll in leaves is approximately 3. They found that this ratio was practically constant for many different species and for different environmental conditions. However, other investigators have found evidence that the ratio depends somewhat upon external conditions.

Working with etiolated corn seedlings, Inman (45) found that, shortly after exposure to light, the chlorophyll *a:b* ratio was very high, approximately 22:1. After an additional 90 min. of light exposure the ratio dropped to 17:1. Similar behavior has been observed in oat seedlings by Burr and Miller (19). The simplest explanation for this behavior would be that chlorophyll *a* is produced first, and that chlorophyll *b* is an oxidation product of chlorophyll *a*. However, this type of oxidation would be very difficult to bring about *in vitro*.

In some of the earlier theories concerning the photosynthetic mechanism, it was assumed that the *a* and *b* components formed a photo-activated oxidation-reduction system, so that the coöperation of both components would be necessary to carry on photosynthesis. Aside from

the difficulty involved in the methyl-formyl oxidation, further evidence that the *a* and *b* components do not function as an oxidation-reduction system is found in the observation of Fischer and Breitner (31) that chlorophyll *b* does not occur in several of the red algae (*Porphyra tenera*, *Bangia fuscopurpurea*, and *Polysiphonia nigrescens*). On the other hand, Beber and Burr (11) observed no photosynthesis in etiolated oat seedlings until long after a perceptible amount of chlorophyll *a* was formed. Their experiments suggested that chlorophyll *b* is necessary for photosynthesis in oat seedlings. Further evidence concerning the degree of interdependence of the two chlorophylls might be obtained from quantum

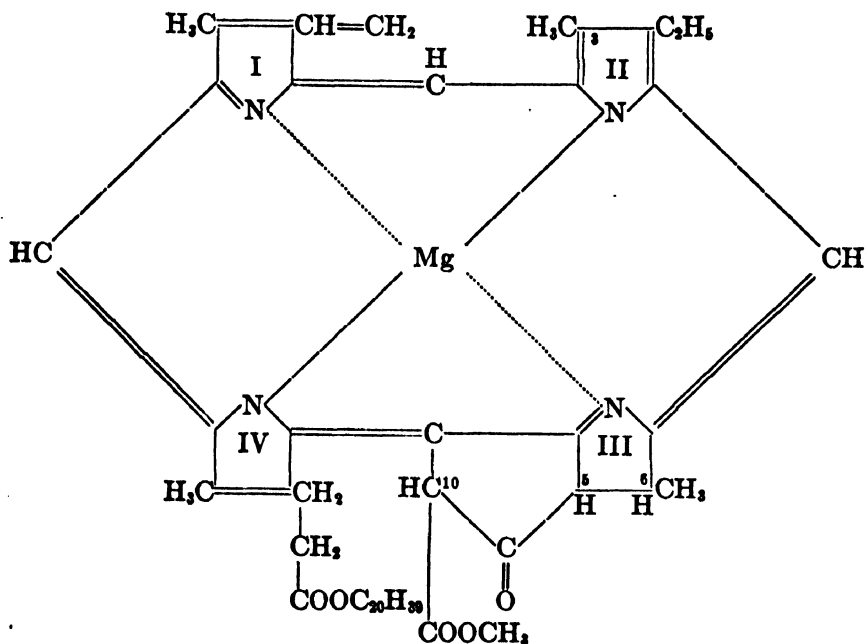


FIG. 9. Fischer's formula for chlorophyll *a* (Steele (73))

efficiency measurements with wave lengths chosen to correspond to the respective absorption maxima of the two pigments.

Stoll (75), on the basis of his own and other investigations, has concluded that the action of both chlorophylls in the photosynthetic process is in large part due to the labile hydrogen atom attached to the carbon atom in the 10-position (figure 9). According to his point of view, the existence of two chlorophyll components may be advantageous to a plant because of the increased range of wave lengths which can thus be absorbed (see figure 1). This might be particularly useful to a plant growing in dim light.

In the chloroplast the position of the absorption maxima for the two

chlorophylls is shifted approximately 200 Å. to the red as compared to the position for the extracted pigments in ether solution. This shift is usually ascribed to differences in the optical properties of the solvents. Albers and Knorr (2) have recently studied the absorption spectra of single chloroplasts in the region from 6640 to 7040 Å. They found evidence for several maxima in the absorption band usually attributed to chlorophyll *a*. They suggested that the several maxima may be due to the presence of compounds between chlorophyll *a* and various intermediates in the photosynthetic process.

The phytol group in the chlorophyll molecule has little influence on the optical properties. Replacement of the phytol group by a methyl group produces only a slight change in the chlorophyll absorption spectrum. The optical properties are due principally to the ring of conjugated double bonds surrounding the central magnesium atom. The phytol group, according to Stoll (75), may serve to make chlorophyll lipid-soluble, thus permitting proper distribution in or on the plastid.

Stoll suggests that, in addition to maintaining the conjugated bond system, magnesium is important in maintaining the proper degree of reactivity with carbonic acid. Chlorophyll forms a complex with carbonic acid *in vitro*, and Stoll, as well as many other investigators, suggests that a similar complex is formed in the plant. As mentioned above (page 825), earlier evidence indicated that the rate of photosynthesis is temperature-dependent even at very low carbon dioxide concentrations. This was regarded as additional evidence for the formation of a carbonic acid (or carbon dioxide) complex with chlorophyll during the photosynthetic process. But the experiments of van den Honert (77) and of Emerson and Green (29) have indicated that the temperature dependence at low carbon dioxide concentrations may be only apparent, and due to complications resulting from the use of buffer mixtures. These observations weaken somewhat the evidence for participation of a carbonic acid-chlorophyll complex in photosynthesis.

It has frequently been observed that chlorophyll in solution is decomposed by the action of light. Albers and Knorr (1, 51) have followed this decomposition in the presence of various gases, by observing changes in the fluorescence spectra of chlorophylls *a* and *b*. Porret and Rabinowitch (63) have studied the bleaching of chlorophyll dissolved in methanol. In the presence of oxygen the quantum yield was approximately 10^{-6} . This value was independent of oxygen concentration over a wide range, but the bleaching disappeared on complete removal of oxygen.

In the absence of oxygen Porret and Rabinowitch (63) found that intense light caused a reversible bleaching of the red absorption band of chlorophyll. Using a 10^{-6} molar solution of chlorophyll in methanol, and a light intensity such that each chlorophyll molecule absorbed about 10 quanta per second, the bleaching of the red band amounted to about

1 per cent. Therefore, assuming the quantum efficiency of the bleaching process to be 1, they estimated an average lifetime for the bleached state of about 10^{-3} sec. The degree of bleaching was approximately proportional to the square root of light intensity. Porret and Rabinowitch suggested that the bleaching was probably due to a dissociation into "dehydrochlorophyll" and a hydrogen atom (perhaps from carbon atom No. 10; see figure 9). In the presence of formic acid the reversible bleaching was increased to 10 per cent. With a dissolved oxygen concentration of 10^{-6} molar, the bleaching with formic acid was reduced about 50 per cent. Apparently the oxygen either formed a complex with chlorophyll or removed the chlorophyll excitation before dissociation could occur.

Rabinowitch and Weiss (65) have found that chlorophyll in methyl alcohol solution is transformed by certain oxidizing agents, particularly ferric chloride, into a yellow product. The chlorophyll could be restored to its original condition by the action of ferrous chloride. The oxidation process was accelerated by light. In the yellow oxidation product the red absorption bands were virtually eliminated, and the blue bands shifted toward shorter wave lengths. A rather peculiar feature of the oxidation process was that the blue band of chlorophyll *b* was changed much more slowly than the red band of *b*, and also more slowly than either the red or blue bands of the *a* component. This suggests that the blue absorption band of *b* may be produced by a chromophoric group different from those responsible for the other absorption bands of chlorophyll. Rabinowitch and Weiss consider it probable that the oxidation of a chlorophyll molecule results in the formation of a positively charged chlorophyll ion, which perhaps then breaks down into a hydrogen ion and dehydrochlorophyll.

It is probable that, in the process of extraction from plant cells, the chlorophyll pigments undergo some sort of chemical change. Some investigators (e.g., Stoll (75) and Franck and Herzfeld (34)) have suggested that, in the chloroplast, chlorophyll may be combined with a protein. Its specific effectiveness in photosynthesis would thus depend upon its attachment to a particular colloidal carrier. In any event, attempts to bring about carbon dioxide reduction by extracted chlorophyll have thus far been unsuccessful.¹⁷ Whether this failure is due principally to changes

¹⁷Baly, Stephen, and Hood (8) have reported the formation of carbohydrates from carbon dioxide and water, with visible light as the energy source. The light-absorbing agent in their experiments was not chlorophyll, but an aqueous suspension of nickel or cobalt carbonate. However, a number of other investigators have tried, without success, to repeat the experiment of Baly, Stephen, and Hood. It may be that these other investigators have failed to duplicate with sufficient exactness the procedure described by Baly *et al.*, but, as Emerson (23) has suggested, it seems reasonable to require that the production of photosynthesis *in vitro* should be capable of repetition before it can be regarded as an established fact.

in the chlorophyll, or to changes in the environment, or both, is as yet an unanswered problem.

Chlorophyll fluorescence

Solutions of chlorophyll emit a bright red fluorescence when illuminated with visible or near ultraviolet radiation. It has been estimated that, under favorable conditions, about 10 per cent of the absorbed radiation may be recovered as fluorescence (36). Chlorophyll in living cells also fluoresces, but much less strongly than solutions of the extracted pigment. The maximum yield for chlorophyll fluorescence in living material is of the order of 0.01 per cent (81). Colloidal solutions of chlorophyll do not fluoresce. The fact that fluorescence occurs in the living cell is often regarded as an indication that chlorophyll is in a dissolved state in the chloroplast. However, the very low intensity of fluorescence in the chloroplast lessens the force of this argument.

Zscheile (94) has determined the fluorescence spectra of chlorophylls *a* and *b* in ether solution. The exciting radiation was supplied by a tungsten filament lamp. The *a* component showed two bands and the *b* component three bands in the region 6300-8200 Å. No observations were made at wave lengths below 6300 Å.

Kautsky and coworkers (49, 50) and Franck and Wood (36) have studied the effect of illumination time on the intensity of fluorescence in living leaves. In Kautsky's experiments the 3660 Å. line of mercury was used as the exciting source, while, in the experiments of Franck and Wood, a tungsten filament lamp with a blue filter was used to produce fluorescence. The results of these two series of investigations, while not identical, showed the same general type of behavior. Following a long period of darkness, the fluorescent intensity from an illuminated leaf is at first very low, but increases rapidly to a maximum after 2 to 5 sec. of illumination. The intensity then diminishes until a constant level is reached after about a minute. At a temperature of 35°C., Kautsky and Marx (50) found that this constant intensity was approximately two-thirds of the temporary maximum value, but at 0.1°C. the intensity remained constant at nearly the maximum value. In the presence of oxygen, the fluorescent intensity was reduced to about half the value observed in the absence of oxygen (49).

Franck and Levi (35) found that weak alcoholic or acetic extracts of leaves, when irradiated in the presence of oxygen, showed a variation in fluorescent intensity similar to that found in leaves.

Kautsky concluded from his investigations that there is an intimate connection between the process of photosynthesis and the process of fluorescence. Earlier investigations (89) indicated that oxygen is necessary for photosynthesis. Consequently, Kautsky attributed the quench-

ing of fluorescence by oxygen to the utilization of chlorophyll excitation energy in the process of photosynthesis. Kautsky and Hormuth (49) suggested that oxygen forms an addition compound with some substance in the chloroplast, and that this compound serves to transfer the chlorophyll excitation energy to carbonic acid, which is thereupon reduced to formaldehyde or carbohydrate.

Kautsky's interpretation is open to question from several points of view. In the first place, recent experiments by Gaffron (39), with *Chlorella*, indicate that oxygen is not essential for photosynthesis. Gaffron observed that when *Chlorella* was illuminated following 15 hr. in darkness in a nitrogen atmosphere, carbon dioxide consumption proceeded normally. However, oxygen production did not occur for some time, presumably because of oxidation of excess intracellular fermentation products.

Secondly, Kautsky used the 3660 Å. line of mercury to excite fluorescence. This wave length is relatively inefficient for photosynthesis (see page 818).

Thirdly, as Emerson (23) has pointed out, a plant exposed to high light intensity is using only a small fraction of the absorbed energy in the photosynthetic process. Consequently, changes in fluorescent intensity might occur quite independently of the photosynthetic process.

Franck and Wood (36), while not considering oxygen as necessary for photosynthesis, concluded that there is a close connection between the processes of photosynthesis and fluorescence. They interpreted the variation in fluorescent intensity as being due to the formation and disappearance of a strongly fluorescent radical.

According to the mechanism of Kautsky and Hormuth (49), it would appear that, at low light intensities, the percentage yield of fluorescence should increase with increasing intensity of the incident light, approaching a maximum value after the attainment of a maximum photosynthetic rate. If this type of relation could actually be established, it would constitute strong evidence for a connection between photosynthesis and fluorescence.

The relation between chlorophyll concentration and the maximum rate of photosynthesis

Emerson (22) and Fleischer (33) have studied the effect of varying chlorophyll concentration on the rate of photosynthesis in *Chlorella*. Emerson grew *Chlorella* in a nutrient solution containing glucose, and varied the chlorophyll concentration by varying the concentration of iron in the nutrient solution. Fleischer varied the chlorophyll concentration in three different ways. In some of his series the iron concentration was varied, while in other series the magnesium or nitrogen concen-

trations were varied. Except for samples deficient in magnesium, Emerson and Fleischer both found that, at high light intensity and abundant carbon dioxide concentration, the rate of photosynthesis per unit volume of cells was approximately proportional to the amount of chlorophyll. When chlorophyll deficiency was caused by insufficient magnesium, Fleischer found an abnormally low rate of photosynthesis, and consequently concluded that magnesium influences the process of photosynthesis in some way other than by its influence on chlorophyll production.

Emerson and Arnold (26) have studied the relation in *Chlorella* between chlorophyll content and the rate of photosynthesis in intermittent light of high intensity. In these experiments the chlorophyll content was varied by varying the light conditions under which the *Chlorella* was cultured. As in previous work (25), they used light flashes which lasted only about 10^{-5} sec., a period which is short compared with the duration of the dark or Blackman reaction (see page 827). Sufficient time was allowed between flashes for completion of the dark reaction, so that light saturation in their intermittent light experiments implied, not that the rate of the dark reaction was limiting, as it is in the case of saturation with continuous light, but that the photochemical mechanism was saturated. Under these conditions the maximum rate was again found to be approximately proportional to the chlorophyll concentration. Emerson and Arnold calculated the ratio between the total number of chlorophyll molecules present in the reaction vessel and the number of carbon dioxide molecules reduced per single light flash. Instead of finding a value of 1 (or of 3 or 4 or 5, as would be expected in case a series of three or four or five alternate photochemical and thermal reactions were required for the photosynthetic cycle), they found a value of approximately 2500. This figure represented the average for all chlorophyll concentrations; its value was apparently independent of chlorophyll concentration. In similar experiments Kohn (52) found that light saturation was reached when only about one chlorophyll molecule in a hundred absorbed one or more quanta in a single flash. Arnold and Kohn (6) have determined the minimum value of the ratio of chlorophyll molecules to carbon dioxide molecules reduced per flash for several different species in different divisions of the plant kingdom. They found the value to lie between 2000 and 4000 in all cases.

Emerson (23, 24) has suggested that carbon dioxide probably does not combine with chlorophyll prior to the photoreaction, and that the ratio of about 2500 probably represents the ratio between chlorophyll and some other internal factor, perhaps the substance which combines with carbon dioxide. However, according to this mechanism, one would expect a very low quantum efficiency, even with low intensity continuous light. The high efficiency values reported by Warburg and Negelein (86), or

even those found by Manning, Stauffer, Duggar, and Daniels (55), would thus be very difficult to explain.

The photosynthetic unit

One way of reconciling the small yield of carbon dioxide reduced per flash with the relatively high quantum efficiencies observed at low light intensities is to assume that light absorbed by a large number of chlorophyll molecules can be made available to a single carbon dioxide molecule. This assumption implies (unless one postulates an extremely long life for excited chlorophyll) that, in the chloroplast, the chlorophyll molecules are distributed in the form of groups or units, each containing a large number of individual molecules. Arnold and Kohn (6), Gaffron and Wohl (40), and Weiss (88) have favored this interpretation. The postulated size of such a unit would depend upon the number of successive photochemical reactions which are required to reduce one carbon dioxide molecule, and also on the number of carbon dioxide molecules associated with each group. Weiss (88) has suggested that a single unit may have carbon dioxide molecules adsorbed on the surface, with one carbon dioxide molecule to each surface molecule of chlorophyll. Assuming four successive photoreactions, it would thus be necessary to have 500 or 600 molecules in the interior for each surface molecule of chlorophyll. Weiss calculated that, if such a unit were spherical, its radius should be of the order of 0.4μ . Globules of this general size have been observed in photographs of chloroplasts (44). However, it is difficult to conceive of energy transmission through a unit of this magnitude without enormous losses in the form of heat.

Gaffron and Wohl (40) obtained additional support for the existence of a photosynthetic unit from approximate calculations in which the data of numerous investigators were used. They found that the maximum photosynthetic rate (light saturation) corresponded to the reduction of one carbon dioxide molecule by each chlorophyll molecule every 10 or 20 sec. This period is approximately 1000 times as long as the average time for the dark or Blackman reaction (25, 26). Assuming a single dark reaction in each cycle, this would indicate a unit of about 1000 chlorophyll molecules for each carbon dioxide molecule.

It has also been suggested (34, 91) that the existence of a photosynthetic unit would account for the absence of a long induction period at low light intensities. If a single chlorophyll molecule were obliged to absorb four or more quanta before oxygen could be liberated, a long induction period would be required at low light intensities. But, if a unit of 500 or 1000 chlorophyll molecules were available for the reduction of each carbon dioxide molecule, the necessary quanta would be absorbed

within a second or two, even at the lowest intensities that have been used in studies of photosynthesis.

If the process of photosynthesis involves a series of photochemical reactions, any thermal decomposition of intermediate products would result in a lowering of the overall efficiency of the process. If one or more of these intermediate products were sufficiently unstable to decompose appreciably within a period of a minute or less, then a plant should be greatly benefited at low light intensities by the coöperation of more than one chlorophyll molecule in the reduction of a carbon dioxide molecule, since the time between successive photoreactions would be shortened in proportion to the number of chlorophyll molecules per unit.

As Gaffron and Wohl (40) have pointed out, a variation in the size of the photosynthetic unit might account for the phenomenon of light adaptation, by which plants of the same species may be conditioned to efficient use of either high or low light intensities. A plant accustomed to high intensities will often photosynthesize more rapidly in bright light than will one accustomed to low intensities, and *vice versa*. A large number of small units would permit more rapid photosynthesis in bright light, while, with weak light, large units would serve to minimize the possible losses due to decomposition of intermediates.

Thermal decomposition of intermediate products might account for the type of behavior shown at low light intensities by the species of purple bacteria which French (37) used in his measurements of quantum efficiency (see page 838). At low light intensities French's measurements indicated a decreasing efficiency as intensity decreased. If thermal decomposition of intermediates was responsible for this behavior, it would be expected that an increase in temperature should increase the rate of decomposition, and thus cause the diminished efficiency to occur at higher light intensities. This effect was actually observed by French (reference 37, figure 5). However, it should be remembered that the change in ΔH is small for the reaction studied by French. The only reason for assuming a series of photoreactions for the process is its apparent similarity to green plant photosynthesis.

Perhaps the strongest argument against the existence of a photosynthetic unit is the difficulty involved in picturing a model which would permit an efficient transfer of energy from every region where visible light could be absorbed to the point where it could be utilized for carbon dioxide reduction.

Franck and Herzfeld (34) considered that the fluorescence of chlorophyll in living plants is an indication of unimolecular dispersion. Since colloidal chlorophyll does not fluoresce *in vitro*, they argue that chlorophyll in units of 500 or more should not fluoresce in the chloroplast.

However, the very low intensity of fluorescence *in vivo* weakens the argument. Rabinowitch¹⁸ has suggested that the weak chlorophyll fluorescence observed in living material may be emitted by a few "misplaced" chlorophyll molecules which may play no part in photosynthesis.

Wohl (91) has discussed in detail various arguments favoring the existence of a photosynthetic unit. He also has suggested several experiments with intermittent light which might add to our knowledge of the photoprocess involved in photosynthesis.

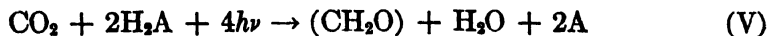
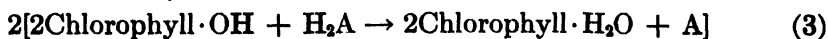
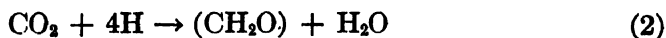
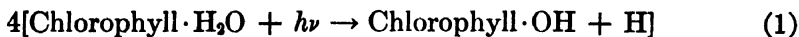
The existence of a photosynthetic unit has thus far been neither proved nor disproved. Its existence would offer an explanation for several different groups of experiments, but on the other hand, various arguments, largely based on physical grounds, can be offered against it.

The mechanism of photosynthesis

Several recent investigators have proposed kinetic mechanisms for the process of photosynthesis, e.g., Arnold (5), Baly (7), Briggs (15), Burk and Lineweaver (16), Franck and Herzfeld (34), and Smith (68). Of these, the mechanism of Franck and Herzfeld is the only one which includes a detailed consideration of the photochemical reactions which may be involved. Other investigators have suggested a variety of chemical mechanisms without going into detail regarding the kinetics of the process (Conant, Dietz, and Kamerling (20), Gaffron and Wohl (40), James (47), Kautsky and Hormuth (49), Stoll (75), van Niel (79)).

In most of these mechanisms it is assumed that the quantum efficiency for the photochemical reaction is 0.25, in accord with the observations of Warburg and Negelein (86). However, the low efficiency values found by recent investigators (see page 835) suggest that the value 0.25 may be too high.

It has also been generally assumed that the photosynthetic process includes a series of four successive photochemical steps, ΔH for a single step being limited to the energy supplied by a single quantum. In van Niel's mechanism, however, the four photochemical steps are assumed to be identical, resulting in each case in the formation of a hydrogen atom; the four hydrogen atoms then presumably bring about the reduction of carbon dioxide to formaldehyde. Van Niel's mechanism is represented by the following equations:



¹⁸ Private communication.

For reaction 1 to be energetically possible, the chlorophyll·H₂O compound would have to be a more intimate compound of chlorophyll and water than in the case of an ordinary hydrate. An alternative way of writing reaction 1 would be

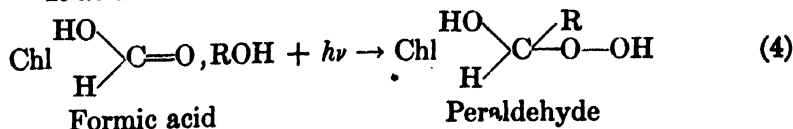
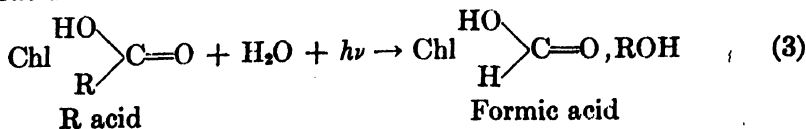
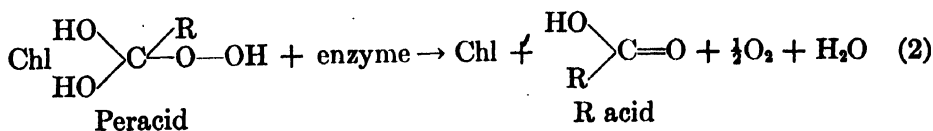
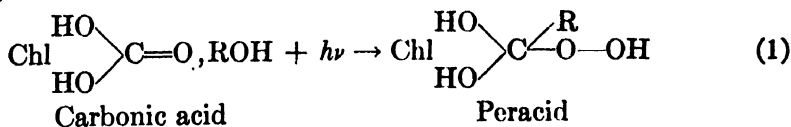


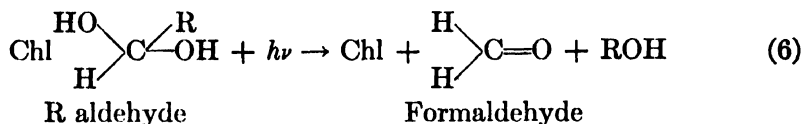
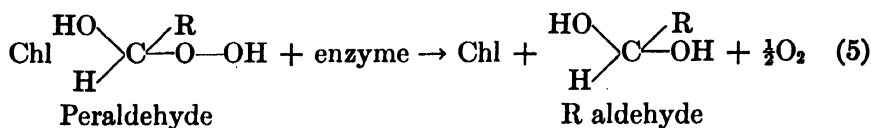
the hydrogen atom thus being split from the chlorophyll portion of the hydrated molecule.

In reaction 3, H₂A would be water in the case of algae and higher plants, and hydrogen sulfide in the case of the green sulfur bacteria.

Without modification this series of reactions could not take place (except perhaps in bacteria) with a quantum efficiency as high as 0.25, since reaction 2 is exothermic to the extent of about 150,000 cal. The energy thus wasted would be nearly equivalent to the total energy supplied by four photons at 7000 Å. For H₂A = H₂O, reaction 3 would be endothermic. The necessary energy would presumably have to be supplied by additional photons, unless reactions 2 and 3 were considered to be coupled in some manner so that the excess energy from reaction 2 could be utilized for reaction 3.

The mechanism of Franck and Herzfeld (34) was designed to avoid the necessity of assuming a photosynthetic unit. They assumed, as did Stoll (75), that carbonic acid forms a complex with chlorophyll. This complex, in turn, was assumed to be combined with an organic molecule ROH, present in abundance. Franck and Herzfeld suggested that ROH may be a protein which forms the main body of the chloroplasts. The following equations represent the forward reactions postulated by Franck and Herzfeld. They state that the equations are suggested as a working hypothesis, not as a final solution.





The two enzyme reactions, in which oxygen is evolved, constitute the temperature-sensitive or Blackman reaction.

According to Franck and Herzfeld, the calculated binding energy of —OH to —O— in the two peroxides is so weak that the —OH radical will be split off whenever the peracid or peraldehyde complexes absorb a photon. At low light intensities the probability of such an absorption would be negligible, because of the speed of the enzyme reactions. But, at intensities corresponding to light saturation in most leaves, they estimated this probability to be about $\frac{1}{10}$. According to their postulation, the photodecomposition of the permolecules into two radicals initiates chain reactions (back reactions in this case), each chain resulting in the decomposition of a large number of permolecules.

With these chains light saturation is thus reached at a much lower intensity than would be required if the rate were limited by the Blackman reactions. By assuming a sufficient chain length ($\sim 10^3$ at light saturation), saturation, both in flashing and in continuous light, can be explained without the assumption of a photosynthetic unit.

Franck and Herzfeld suggested that, after a long dark period, much of the chlorophyll may be attached to intermediate respiratory products, probably plant acids. Illumination could then cause photosynthesis, as in the case of chlorophyll-carbonic acid or chlorophyll-formic acid complexes. However, according to Franck and Herzfeld, photooxidation of these plant acids, probably by a chain mechanism, should also take place to a large extent. Until the accumulated respiratory products were exhausted, this oxygen consumption would largely counterbalance the photosynthetic oxygen production, thus producing an induction period. Increased probability of oxidation at high light intensities would cause a more noticeable underproduction of oxygen at high intensities than at low intensities, in agreement with experimental results (53).

The kinetic equations derived by Franck and Herzfeld are in reasonable agreement with experimental facts. However, this cannot be considered as a criterion for the correctness of the mechanism, since equations derived by other investigators on the basis of various mechanisms are also in fairly good agreement with experimental results.

The reverse chain reactions of Franck and Herzfeld have been subjected

to some criticism (91). Aside from doubts concerning this part of their mechanism, it is evident that to account for the high efficiencies found by Warburg and Negelein, the various forward reactions in the mechanism of Franck and Herzfeld would have to proceed with remarkable efficiency. Not only would the quantum efficiencies for each photoreaction have to be nearly unity, but the intermediate products would have to remain practically unchanged during the periods between the absorption of successive quanta by a single chlorophyll molecule. This period, according to calculations of Gaffron and Wohl (40), was about 10 min. in many of the experiments of Warburg and Negelein. But Franck and Herzfeld explained the induction period by assuming that, in the dark, a considerable fraction of the chlorophyll molecules become attached to intermediate respiratory products. The experiments of McAlister with wheat (53) indicated that 10 min. in the dark is sufficient to produce a noticeable induction period. Thus, in its present form, the mechanism of Franck and Herzfeld can hardly be reconciled with the results of Warburg and Negelein. It could much more easily account for the efficiencies found by Manning, Stauffer, Duggar, and Daniels (55). But, if the maximum quantum efficiency for photosynthesis is actually only 0.06 instead of 0.25, then there is no very good reason for choosing a mechanism involving four photoreactions, rather than one involving five or possibly more reactions.

In some respects it may be more desirable to postulate a mechanism involving only a single photoreaction, as in van Niel's mechanism (79). This result could also be obtained in a manner quite different from that suggested by van Niel. The following scheme indicates a possible mechanism of this type.

In the series of substances $A_1, A_2, \dots, A_{n-1}, A_n$, carbon dioxide or carbonic acid is represented by A_1 and formaldehyde or other product is represented by A_n , with the other symbols representing intermediate substances. Assuming for simplicity that there are three intermediates, the following series of changes might conceivably take place:



The overall equation would then be $A_1 + 4h\nu \rightarrow A_5$. Water, oxygen, and other possible reactants are ignored in the above equations. Reactions 1 and 2 would presumably be enzyme reactions. The Blackman reaction might consist of one or more reactions like reaction 1 or 2, or it might be due to intermediate reactions not included in this or the following scheme.

To avoid postulating an enzyme reaction involving carbonic acid, one might use the following type of scheme:



The sum of these reactions again gives the equation $A_1 + 4h\nu \rightarrow A_5$. Disproportionation reactions similar in principle to 2' and 3' are probably necessary in the production, by a plant, of such compounds as fats and oils, where presumably much of the energy comes from the oxidation of glucose.

If the maximum quantum efficiency is much lower than 0.25, many mechanisms of this type are possible, particularly ones involving more than three intermediate products.

With a mechanism of the type just proposed, a relatively high quantum efficiency could be maintained at very low light intensities without necessitating stable intermediate substances, such as would be necessary with a mechanism like that of Franck and Herzfeld.

Perhaps the principal value of this discussion has been to give an indication of how little actually is known concerning the chemistry of the photosynthetic process. When such entirely different mechanisms can possess even a small degree of plausibility, the need for further definite information becomes evident.

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THE SORPTION OF OXYGEN BY SEVERAL METAL CHROMITES

J. C. W. FRAZER AND LLEWELLYN HEARD

Department of Chemistry, The Johns Hopkins University, Baltimore, Maryland

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The study made by C. G. Albert (2) of the sorption of oxygen and of carbon monoxide by a copper chromite catalyst indicated that a similar study of the sorption of oxygen by several metal chromites might be of interest. The opinion that alternate oxidation and reduction of chromite catalysts tended to render them more active had been suggested by limited experience with some chromites, but it was not known whether chromites prepared by other methods would sorb greater or lesser quantities of oxygen. However, a very good basis for surface comparison was at hand, since Lory (3) had arrived at a figure of 4.11×10^{18} surface atoms of chromium per gram of a copper chromite catalyst, this value having been obtained by leaching chromic acid from the oxidized catalyst with boiling water and titrating with sodium thiosulfate.

APPARATUS AND TECHNIQUE

The apparatus and technique employed in making these measurements, as well as the preparation and purification of gases involved, were as described by Albert (2), with the exception that the volume measurements of the catalyst bulb were made, at the several temperatures, with tank nitrogen instead of helium, it having been determined that, as far as this purpose was concerned, no differences could be observed. An oxygen pressure of 350 mm. of mercury was likewise adopted. Sorption data were plotted in terms of cubic centimeters of oxygen sorbed per gram of catalyst versus time in minutes. From the rate isotherms so obtained, energies of activation associated with the sorption process were calculated.

THE CATALYSTS

The general scheme of preparing the catalysts consisted in obtaining a crystalline intermediate of the type $(\text{NH}_4)_2\text{M}(\text{CrO}_4)_2 \cdot 2\text{NH}_3$ (1) (where M is a bivalent metal), drying, decomposing thermally at as low a temperature as possible (200–300°C.), leaching with hot 6 N hydrochloric acid until no further test for metal ion could be obtained, washing, and drying.

While the use of leach-acid may have influenced the catalyst otherwise, the primary purpose was to dissolve any undecomposed material and any

metal oxide present, since the oxide would have been variously subject to reduction by carbon monoxide with consequent inaccurate sorption results.

The chromites studied are regarded as insoluble in concentrated hydrochloric acid, although in their oxidized state, concerning which little beyond conjecture is available, chromic acid may be leached from them by water.

Chromites made in this manner take up water and other liquids. It was the practice, immediately upon sealing them into the system, to raise the temperature to 300°C. and then carefully to evacuate to 1–10 mm. of mercury. Under these conditions from 48 to 72 hours were required to dry them.

The object of using the crystal intermediate method was that uniformity of composition would always be found in pure crystals, giving rise to catalyst reproducibility.

TABLE 1
Conversion temperatures of carbon monoxide by chromites

CHROMITE	LOWEST CONVERSION TEMPERATURE	LOWEST TEMPERATURE OF COMPLETE CONVERSION
	°C.	°C.
CuCr ₂ O ₄	85	185
ZnCr ₂ O ₄	100	210
CoCr ₂ O ₄	68	210
NiCr ₂ O ₄	78	141
BeCr ₂ O ₄	105	186

The catalysts employed were the chromites of copper, zinc, cobalt, nickel, and beryllium. Those of copper, zinc, and cobalt were prepared by the scheme of Briggs (1), but nickel chromite by the same method was so finely divided that it could not be leached with 6 *N* hydrochloric acid without being peptized and carried away in the leach-acid. Its preparation consisted in dissolving nickelous pyridino dichromate (4), NiCr₂O₇·4Py, in concentrated ammonium hydroxide, removing the pyridine layer which separated, and crystallizing. This product required heating to redness before any appreciable decomposition could be observed. The second leaching failed to give a test for nickel. Beryllium chromite was prepared by the thermal decomposition of (NH₄)₂Be(CrO₄)₂. It was a fine gray powder.

For each catalyst the temperature at which conversion of carbon monoxide to carbon dioxide began, and at which it was complete and continuous, was determined in the apparatus described by Lory. These operations established the ranges within which, at 25°C. intervals, sorption measurements should be made. The lower and upper limits are shown in table 1.

Before sealing a catalyst into the system the sample was placed in a Pyrex carbon dioxide trap within an electric resistance furnace and, when the temperature had come to equilibrium at 200°C., a slow stream of tank oxygen was passed over it for 2 hours. The object was to oxidize the catalyst surface completely. After sealing into the system the chromite was reduced in an atmosphere of carbon monoxide prior to making each measurement.

EXPERIMENTAL RESULTS

The data of the sorption of oxygen by the several chromites employed are indicated graphically in figures 1 to 5, inclusive, while the calculated values of E are given in tables 2 to 5.

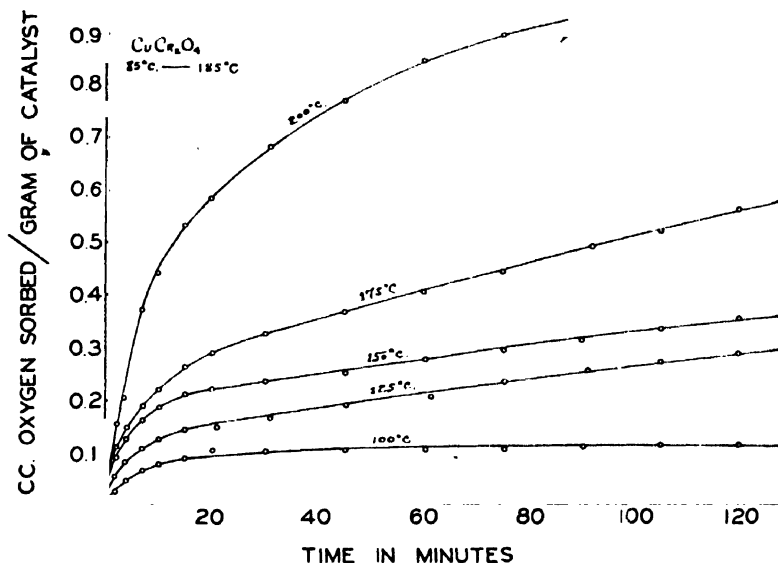


FIG. 1. Sorption of oxygen by copper chromite

It is interesting to note that while this sample of copper chromite sorbed approximately four times the amount of oxygen sorbed by Albert's catalyst, under the same conditions, the values for the energies of activation are in quite good agreement.

A sample of 5.1596 g. of this same batch of copper chromite was brought to 200°C. in a carbon dioxide trap, as indicated above, and a stream of tank oxygen was passed over it for 2 hours. The temperature rose at once to about 600°C., and then gradually fell during the next 10 to 15 minutes. At the end of the treatment the sample was leached with hot water until no further chromium could be found in a drop of the leach-water. It yielded 0.0815 g. of chromium, giving a figure of 1.84×10^{20} surface atoms

of chromium per gram of catalyst, which, divided by Lory's figure, indicates an oxidizable or active surface 44.77 times greater than that shown

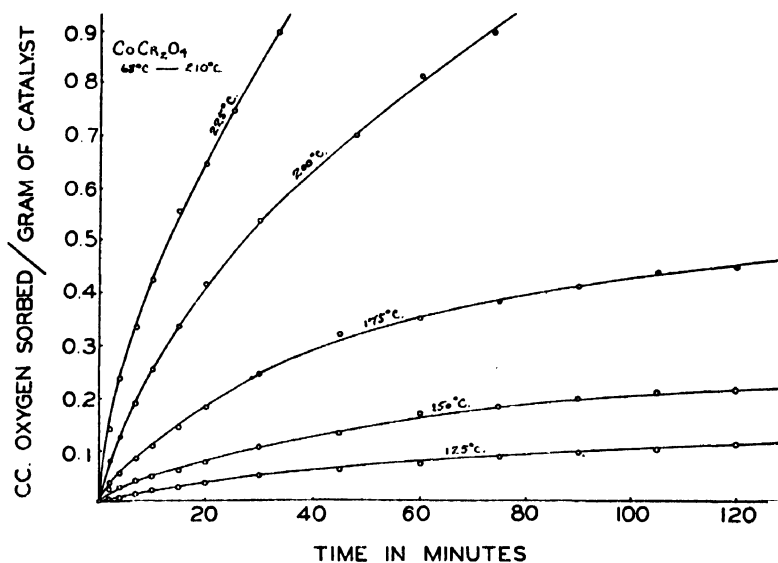


FIG. 2. Sorption of oxygen by cobalt chromite

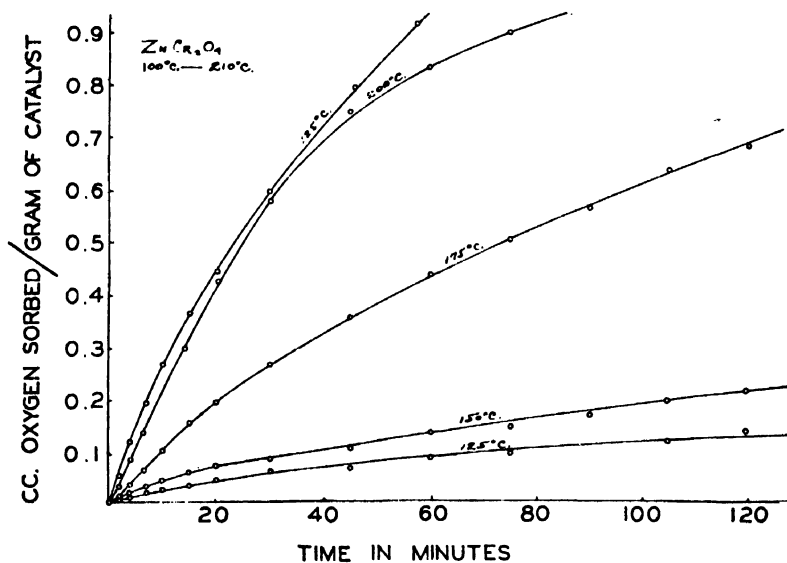


FIG. 3. Sorption of oxygen by zinc chromite

by Albert's catalyst. The apparent discrepancy between the amount of oxygen sorbed by the catalyst within the system at 200°C. and the enormity of the surface indicated by the leaching method is readily explained. The

pressure maintained in the system was 350 mm. of mercury, whereas oxidation prior to leaching was carried out at atmospheric pressure. Thus more

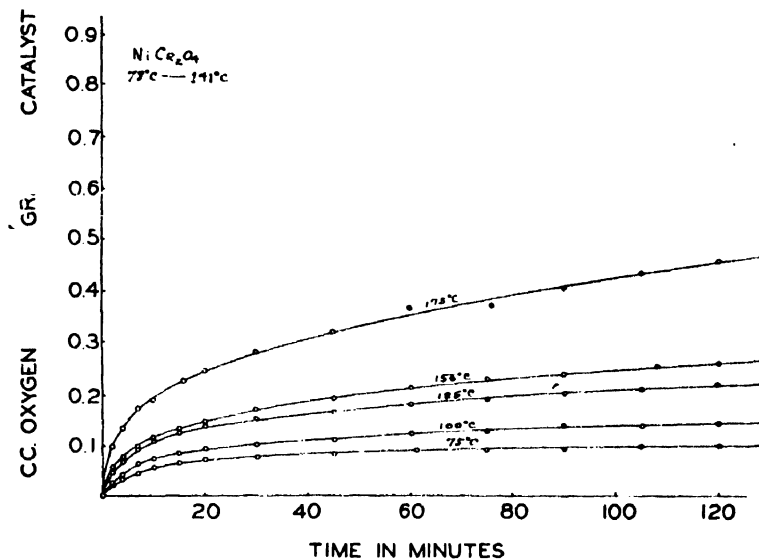


FIG. 4. Sorption of oxygen by nickel chromite

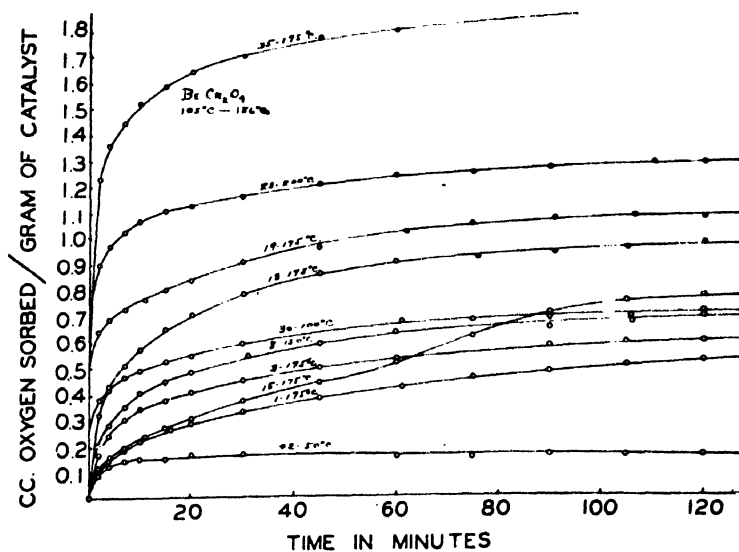


FIG. 5. Sorption of oxygen by beryllium chromite

rapid oxidation accompanied by rapid increase in temperature produced in turn still greater oxidation, both sorption measurement and heat treatment being conducted over identical time intervals. Assuming the forma-

TABLE 2

Activation energies of the sorption of oxygen by copper chromite

AMOUNT SORBED	E (IN KILOGRAM-CALORIES)						
	100-125°C.	100-150°C.	125-150°C.	125-175°C.	150-175°C.	150-200°C.	175-200°C.
cc.							
0.02	15.58	16.94					
0.04	12.63	13.58					
0.06	12.00	11.31					
0.08	12.07	10.87					
0.10	13.44	11.92					
0.14			12.55	8.78			
0.18			18.91	12.66			
0.22			16.41	13.22			
0.26			9.17	13.21			
0.30			6.32	12.08			
0.33					18.36	22.83	
0.36					15.85	22.99	
0.39							33.39
0.42							34.03
0.45							34.19
0.48							35.46
0.51							33.26
0.54							32.42
0.57							31.60

TABLE 3

Activation energies of the sorption of oxygen by cobalt chromite

AMOUNT SORBED	E (IN KILOGRAM-CALORIES)						
	125-150°C.	125-175°C.	150-175°C.	150-200°C.	175-200°C.	175-225°C.	200-225°C.
cc.							
0.02	16.08	14.36					
0.04	13.87	14.58					
0.06	13.80	15.19					
0.08	15.76	16.32					
0.10	17.72	17.11					
0.12			16.92	17.87			
0.14			16.93	17.95			
0.16			17.70	18.39			
0.18			19.20	19.14			
0.20			20.89	20.08			
0.24					19.32	17.22	
0.27					19.86	17.36	
0.30					20.39	17.25	
0.33					20.85	17.59	
0.36					22.06	17.79	
0.39					24.50	18.65	
0.42					25.24	19.60	
0.45					27.51	20.43	
0.50							14.34
0.55							14.53
0.60							14.38
0.65							14.33
0.70							14.34
0.75							14.48
0.80							14.65
0.85							15.05
0.90							15.52

TABLE 4

Activation energies of the sorption of oxygen by zinc chromite

AMOUNT SORBED	E (IN KILOGRAM-CALORIES)				
	125-150°C.	125-175°C.	150-175°C.	150-200°C.	175-200°C.
cc.					
0.02	7.07	8.32			
0.04	8.18	9.72			
0.06	10.59	12.32			
0.08	10.96	14.15			
0.10	11.15	15.09			
0.12	9.80	15.64			
0.14	9.09	14.65			
0.16			24.51	18.89	
0.18			24.94	19.48	
0.20			25.32	19.81	
0.22			25.39	19.93	
0.25					14.65
0.30					15.02
0.35					16.12
0.40					16.69
0.45					17.24
0.50					17.87
0.55					18.59
0.60					18.53
0.70					18.72

TABLE 5

Activation energies of the sorption of oxygen by nickel chromite

SORBED	E (IN KILOGRAM-CALORIES)						
	75-100°C.	75-125°C.	100-125°C.	100-150°C.	125-150°C.	125-175°C.	150-175°C.
cc.							
0.02	1.151	6.33					
0.04	3.378	5.93					
0.06	4.961	6.46					
0.08	11.03	10.17					
0.10	13.91	14.11					
0.12			16.14	9.92			
0.14			18.23	11.77			
0.16			14.51	10.70			
0.18					6.62	13.45	
0.20					7.00	14.12	
0.22					8.42	14.89	
0.24							23.27
0.26							23.54

tion of monomolecular layers in both the Lory and the present form of chromite, there is far from enough information to relate surface to oxygen sorbed over short time intervals.

DISCUSSION

Many of the metal chromites may be prepared through the Briggs' intermediate, and those so prepared have large surfaces as compared with the Lory catalyst.

The energies of activation of those chromites studied compare favorably with the values obtained for copper chromite by Albert.

Because of the peculiar action of beryllium chromite it was not possible to obtain any reliable energy values. The first sorption measurement was conducted at 175°C., and when an effort was made to duplicate the rate isotherm a curve revealing greater sorption resulted. A third run at the same temperature gave a curve lying still higher. Curves representing runs 1 and 3 are shown on the graph as 1-175 and 3-175. A run was then made at 100°C., and no oxygen appeared to be taken up. Half a dozen runs were next made, alternately, at 150°C. and 175°C. Each successive curve fell higher than the preceding one for the same temperature.

After run 13 had been made at 175°C., where sorption occurred to approximately twice the extent in run 1, it was decided that the catalyst might be brought to a condition of maximum sorption by oxidizing it at atmospheric pressure and at 200°C. This treatment caused it to lose temporarily some of its sorptive capacity, and the run which followed, at 175°C., gave a curve lying almost on top of curve 1. Thereafter its sorptive capacity began to increase again, curve 15 indicating this tendency.

Several runs were then made alternately at 175°C. and 200°C.; two of the results are shown in curves 19 and 23. After run 35, at 175°C., when beryllium chromite was sorbing about thirty times the amount of oxygen sorbed by Albert's catalyst and about five times that sorbed by the copper chromite sample used in these measurements, several runs were made at lower temperatures; finally, run 42 was made at 50°C. with the results shown in the graph. It may be remembered that run 4 was made at 100°C. without measurable sorption occurring.

This points to the already-proposed view that alternate oxidation and reduction of a chromite catalyst tends to increase its activity,—certainly in the case of beryllium chromite. It is not known whether more surface was being progressively activated or whether the particles of catalyst were breaking into more finely divided particles. In any event the apparent volume of the catalyst in the tube appeared to be unchanged.

After the beryllium chromite was removed from the system it was retested in the Lory apparatus. The temperature of initial conversion of carbon monoxide to carbon dioxide had fallen to 38°C., while the temperature of complete conversion had risen to 192°C.

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NEW BOOKS

Crystal Chemistry. By CHARLES W. STILLWELL. 431 pp. New York: McGraw-Hill Book Company, Inc., 1938. Price: \$4.50.

Crystal chemistry is a new branch of chemistry. The author, in his preface, defines it as follows: "Crystal chemistry is the study of (1) the laws governing the arrangement of atoms in solids and (2) the influence of the arrangement and electronic structure of the atoms upon the physical and chemical properties of the solid." It had its beginning only about ten years ago when Pauling and Goldschmidt, independently, began the correlation of the accumulated data and results of crystal structure analysis. The principles of crystal chemistry already make necessary a revision of some of the basic concepts of chemistry. Hence the importance of this new science to every chemist, both in research and teaching, is only too obvious.

The reviewer wishes to state immediately that the author has produced a very excellent book which can be most enthusiastically recommended. Many have probably read the author's splendid series of papers on this subject which appeared in the *Journal of Chemical Education* in 1936-37. These papers form the basis of parts of four chapters. The chapter titles are as follows: I, Introduction; II, The Sizes of Atoms and Ions; III, The Structures and Properties of the Elements: The Metallic State; IV, The Nature of Alloys; V, The Structures of Binary Compounds; VI, The Properties of Binary Compounds; VII, The Structures of Ternary Compounds; VIII, The Structures of the Silicates; IX, The Structures of Werner Compounds; X, Isomorphism, Mixed Crystals, Polymorphism; XI, The Structures of Organic Crystals; XII, Natural Fibers; XIII, Synthetic Fibers.

No space is devoted to discussion of the methods of crystal analysis. In the introduction the author first very briefly discusses a few fundamentals of crystallography. The remainder of the chapter is then spent in giving the reader a brief and suggestive sketch of crystal chemistry. In fact the author points out, in his preface, that the material of the introduction is intended for use in the introductory course in chemistry. The fundamentals outlined in the introduction are then developed in greater detail in the remainder of the book, making it as a whole very suitable for advanced courses.

The book contains an immense amount of data in the form of 122 tables. In addition there are 72 figures (charts, diagrams, photographs, etc.) which are almost without exception well chosen and well reproduced. The list of references is not exhaustive, but it is sufficiently complete to form a basis for a more detailed study of the subject. There appear to be very few errors of a factual nature, but several obvious typographical errors have crept in.

In conclusion, the reviewer again wishes to state that all chemists, and readers interested in chemistry, will find this an excellent and timely book.

HAROLD P. KLUG.

Grundzüge der Theorie ungesättigter und aromatischer Verbindungen. By E. HÜCKEL. 21 x 15 cm; 160 pp. Berlin: Verlag Chemie, G.m.b.H., 1938. Price: 6 RM.

This is a reprint of an article appearing in *Zeitschrift für Elektrochemie* (volume 43). The author attempts to explain with a minimum of mathematics the ideas on which the recent theories of "resonance" are based, and the principal results which have

been obtained. One of his first points is that the analogy between "resonance" in molecules and resonance in the theory of forced oscillations is remote; he therefore prefers to use "mesomerism," a word originally suggested by Ingold.

The first half of the book explains briefly the pair and orbital methods of approximation to the energy of formation of polyatomic molecules, and applies them to ethylene and to benzene and other ring compounds. A chapter on free radicals follows, and some interesting speculations on di-radicals are mentioned. The subject matter of chapter V is the reactivity properties of various unsaturated and aromatic compounds. Very simple calculations, for example, give the most likely point of attachment of a first and then a second halogen atom to a number of unsaturated rings or conjugated chains. Other more complicated reactions are also considered. The last chapter gives a brief sketch of the theory of ring compounds in which one of the corner atoms is not carbon. Polar effects of unknown size here make the theory very uncertain.

In the opinion of the reviewer, several topics have been omitted which should have been included. One of the early chapters should have explained the difference between the valency state of carbon and the normal state, and hence lead up to an estimate of the energy of reorganization (Van Vleck's theory). This chapter, or another, should have given a brief account of the localized bonds. Another possible omission is that no estimate of the resistance of the ethylene molecule to twisting is made, although the most stable position is stated to be planar.

A further criticism is that no matter in what form comparisons of "calculated" and observed energies of formation of long series of aromatic and unsaturated molecules are presented, far too good an impression of the accuracy of the theory is given. What is being tested by these comparisons is not the theory, but the constancy of bond energies from molecule to molecule. When the molecule is mesomeric, as a matter of observation, some of the bonds gain slightly in stability, and the theory of mesomerism in its present form seems to offer a convenient semi-empirical method for estimating these gains. Unless this is made very clear to the general reader, he will get the impression that the theory is almost rigorously precise, whereas all that may be said at present is that apparently it gives precise results.

The book is recommended because those topics with which it deals are covered very well. Any later book on mesomerism will be able to make considerable use of the present work. It would seem desirable, however, that in a more extended account of the subject other important topics should be mentioned, such as the difference between the valency state of carbon and the normal state, localized bonds, and a more detailed statement of the resistance of molecules such as that of ethylene to twisting. More emphasis might also be laid on the semi-empirical character of some of the calculations of the present time.

W. G. PENNEY.

Duodecimal Arithmetic. By GEORGE S. TERRY. 407 pp. New York: Longmans, Green and Co., 1938. Price: \$7.50.

It has often been pointed out that the operations of arithmetic would be simplified in many respects if our counting were based on some other number than ten. The base twelve, in particular, has important advantages in its divisibility by 2, 3, 4, and 6. One must be an enthusiast, nevertheless, in order to look hopefully toward widespread adoption of a new system of numeration for the purposes of school, commerce, and science. The author of *Duodecimal Arithmetic* is such an enthusiast, and has given as favorable a presentation of the case for the duodecimal system as can well be imagined.

The verbal argument is brief, temperate, and judicious. The fundamental

arithmetical processes are explained and illustrated in a notation using the digits 0, 1, 2, ... 9, together with the symbols X and E, or modifications of them, for the numbers ordinarily called ten and eleven. The equation $34 + 121 = 155$, for example, becomes $2X + X1 = 10E$. The introduction is followed by an extensive set of tables including powers and roots, reciprocals, logarithms, and the natural values and logarithms of trigonometric functions, largely to nine places of duodecimals, designed to facilitate an adequate trial of the notation for purposes of actual calculation. The text and tables, excellent in arrangement, convenient to the hand and agreeable to the eye, will be interesting and instructive to many students who examine them with less serious purpose than the ultimate reform of all arithmetic.

DUNHAM JACKSON.

Expresion de la Reaccion y Calculos Potenciometricos en la Determinacion del pH.

By DOMINGO GIRIBALDO. 271 pp. Montevideo: Casa A Bareiro y Ramos, 1937.

This book is divided into three parts. In the first part, involving eight chapters, the reaction (pH) of aqueous solutions is discussed with emphasis on the expression $pR = \log H^+ - \log OH^-$. The dissociation and neutralization curves of ampholytes are described in detail. The second part (nine chapters) deals mainly with principles of potentiometry, the calculations involved, and the potentiometric determination of pH with the hydrogen, quinhydrone, and glass electrodes. The last part presents tables with explanatory notes which are useful in the calculations.

The book is quite up to date and is a good addition to the literature on this subject in the Spanish language.

I. M. KOLTHOFF.

Qualitative Analyse mit Hilfe von Tüpfelreaktionen. By FRITZ FEIGL. 3rd edition. 554 pp. Leipzig: Akademische Verlagsgesellschaft, 1938. Price: bound, 30 RM.

Feigl's book does not need a recommendation. The rapid appearance of the third edition after the second one (1935), with the English and Russian translations of the latter, shows without doubt that the book is universally considered a standard work. It occupies a unique place in qualitative analysis. It serves as a guide for further research in the development of new (mainly) organic reagents and tests and it contains a wealth of information regarding the identification and separation of inorganic and organic ions and molecules.

To the theoretical part have been added chapters on "fluorescence analysis and spot reactions" and "effect of substitutions by heavy groups on solubility." The practical part occupies about 400 pages and gives an extensive review of the detection of inorganic cations and anions, of systematic schemes of separation, of the detection of elements and reactive groups in organic compounds and of a number of organic substances. The last chapter deals with the application of spot tests to purity tests and detection of traces of various constituents in minerals, ores, alloys, etc. Finally, an extensive alphabetical table is given in which the reagents and sensitivities of the reactions of the various inorganic and organic components are summarized with references to pages in the text.

The book is a tribute to Feigl's pioneer work in the field. It is a sad coincidence that the publication of this third edition occurred at the time when the author with many other scholars was dismissed from the University of Vienna for racial or political reasons. The reviewer expresses the wish that chemists whose views and outlook are determined mainly by the search for truth will cooperate in finding a deserving position for the author which will enable him to continue his important researches in a truly scientific environment.

I. M. KOLTHOFF.

Numerical Problems in Advanced Physical Chemistry. By J. H. WOLFENDEN. 227 pp. London: Oxford Press, 1938. Price: \$2.75.

The 133 problems which make up this list have been selected from the original literature to illustrate the principal divisions of physical chemistry. In the reviewer's opinion the selection has been made wisely and with remarkably little bias. The essential data of each problem are accompanied by a brief but valuable discussion of the immediate background of the subject. The usefulness of the book is greatly increased by the inclusion of references to the original literature, to specialized monographs, and to a number of the better known texts of physical chemistry. Answers to the problems are furnished at the end of the book.

Any independent student of general physical chemistry should find this book helpful and stimulating. In this country it will probably be used most extensively by candidates for the doctor's degree in reviewing their elementary physical chemistry in preparation for examination.

ROBERT LIVINGSTON.

Newer Methods of Volumetric Chemical Analysis. By E. BRENNKE, N. H. FURMAN, K. STAMM, R. LANG, and K. FAJANS; WILHELM BÖTTGER, Editor. Translated by Ralph E. Oesper. 268 pp. New York: D. Van Nostrand Company, Inc., 1938. Price: \$3.75.

This volume is the English translation of the second German edition of *Neuere massanalytische Methoden*, one of the series *Die chemische Analyse*. The book is a collection of discussions of recent developments in volumetric analysis embracing the following topics: elimination of the titration error in acidimetric and alkalimetric titrations, ceric sulfate as a volumetric oxidizing agent, alkaline permanganate solution as volumetric oxidizing agent, iodate and bromate methods (including Manchot's bromometric method), chromous solutions as volumetric reducing agents, oxidation-reduction indicators, and adsorption indicators for precipitation titrations. Comprehensive bibliographies are appended to each section. As stated by the editor in the preface, "These topics have been treated with two objectives in mind: (a) exposition of the theory underlying the new method, so that an insight may be gained into the reasons for the way in which the subject has been developed, and (b) the presentation, so far as possible, of an exact set of directions for the performance of particular analyses."

In reading this book one cannot but be struck by the important rôle played by physicochemical principles in the development of modern methods of chemical analysis. The topics treated do not exhaust the field and one might wish that other phases of the subject (for example, induced reactions) had been included.

The translation has been excellently done. A number of minor errors of typographical nature were noted. "Quinquevalent" has been spelled "quivalent." In the footnote on page 99, the journal reference should be "Z. angew. Chem.," not "Z. anorg. Chem."

E. B. SANDELL.

Photoelements and their Application. By BRUNO LANGE. Translated by Ancel St. John. New York: Reinhold Publishing Corp., 1938. Price: \$5.50.

This book is the first covering the whole field of semiconduction photo cells. About 238 references are cited and commented upon.

The book is divided into two sections. The first deals with the development and properties of the photoelements and the second with the applications. The first section gives an integrated picture of the development and properties of what

Dr. Lange calls "photoelements", including "barrier-layer cells, photovoltaic cells, crystal cells, Becquerel cells, etc."

The brief historical development is followed by a review of the various theories concerning the semiconductor photoeffect. The Shottky (barrier film) and the Teichmann (field funnel) theories are correlated, the electrochemical theory discarded, and the electron diffusion theory, using an insulating layer, stressed. It seems unfortunate to the reviewer that the difference of the insulating layer and the barrier layer is stressed. Although the cuprous oxide front wall cell mentioned on page 73 does not show unipolar conductivity, both the German electrocell and the Weston phototronic cell do show unipolar conductivity. Both of these are front-wall selenium cells. The conclusion would seem that the idea of a barrier film cannot be dismissed so easily. In explaining the photo E.M.F. by electron concentration gradients only the concentration in the semiconductor and the insulating layer are considered, although there would be considerable electron concentration in the metal layer above it. It is this factor that the barrier layer has tried to explain.

The chapter on physical properties coordinates a vast amount of literature of the past few years. It will be very valuable to anyone desiring to review these when time for review is limited. The characteristics of the cell—photocurrent, photopotential, and cell resistance as related to intensity of illumination as well as to each other—are described and the curves given. The effect of temperature, wave length of incident light, polarized light, x-rays, cathode rays, and magnetic field are discussed, similarly the frequency relations and capacitive properties. The stability and fatigue values are clearly separated from each other. The effect of fatigue is eliminated in stability measurements by allowing a two-hour dark recovery period before measurement. Of interest to physicists may be the method applied in determining the work function and the threshold wave lengths by indirect measurements.

The first section of the book serves as an excellent bibliography up to 1935; however, a great deal of work has been done since that date and this is not covered by the translator.

The second section deals entirely with construction and applications. The details on construction are very incomplete and would offer little help to anyone interested in this art.

The description of applications is, however, very complete. The section is very similar to a manufacturer's publication, and as such stresses particularly the apparatus of the German companies. The section is, however, very readable and has many interesting suggestions for manufacturers or chemists interested in control instruments.

Exposure meters for photographic control (some semiautomatic on motion picture cameras), for copying, and for photomicrographic use are described. Transparency and density meters, micro- and spectro-photometers, reflection and gloss meters are common uses. Of great interest to the chemist is the accurate measurement by differential means of absorption of light in colorimetry. The use for analytical work of this type is rapidly growing. The application of photoelement cells is described for long distance transmission of circular or straight scales, for industrial cases where the position of the original instrument is fixed. Other applications include auxiliary control for balances, switching and signal devices, etc. In some of these cases the advantages of the photoelement as opposed to the photoelectric vacuum tube are pointed out.

In conclusion the author suggests uses in the fields of chemistry, physics, astronomy, bioclimatology, meteorology, oceanography, hydrography, medicine, and electrical engineering and also as a source of energy.

The latter half of the book is primarily an advertising medium and should be treated as such. The first half is an interesting integration of the knowledge and theory of the semiconductor photocell at the time the book was written.

JOHNSTONE S. MACKAY.

The Catalytic Action of Surfaces. By J. E. NYROP. Second edition. 103 pp. 20 x 27 cm. Copenhagen, Denmark: Levin and Munksgaard, 1937. Price: 10 Danish krone.

The thesis that the author attempts to develop and support by experimental and theoretical arguments is stated in the following two postulates: "Postulate A. In a chemical reaction furthered considerably by the presence of a surface the surface is at the temperature in question able to ionize those molecules among the reactants most difficult to ionize and the surface will cause a strong adsorption as ions formed are attracted by the surface. Postulate B. A surface able to ionize molecules of a gas or liquid and hence able to yield a strong adsorption produces an increased adsorption when the molecules are substituted by others having a lower ionization potential assuming that all other conditions are the same."

Since new points of view in catalysis are always welcome, this book with its eighty-three references and its partial summary of experimental work in catalysis will probably be found interesting to many readers. To all it should prove thought-provoking. However, in the reviewer's opinion, the book is unconvincing and in some respects carelessly written.

The attempted substantiation of the ideas of postulates A and B by presentation of catalytic data is frequently marred by an evident lack of critical judgment or a careless scrambling of experimental results. The following excerpt from page 23 will suffice as an illustration: "When hydrogenation of the (carbon) monoxide takes place on copper, methane is produced and, as the ionization energy of these products is between 13.7 and 15 volts, none of them take up the space of the surface zone preferentially. If three volumes of hydrogen and one volume of nitrogen pass over a surface of nickel or one of iron at certain temperatures and pressures ammonia is produced and the best result is obtained when the adsorption takes place in the proportion of 3:1. In accordance with technical results this takes place on iron."

To appraise this statement properly one must bear in mind that copper is ordinarily considered incapable of hydrogenating carbon monoxide to methane, that the ionization potentials of H_2O , CO , CH_4 , and H_2 are 12.7, 14.1, 14.5, and 15.37 volts, respectively, and that the separate adsorption measurements for hydrogen and nitrogen on iron catalysts do not reveal a 3:1 ratio at any temperature at which the synthesis of ammonia takes place, as far as the reviewer has been able to ascertain. No source of information was cited in connection with the paragraph from which the above quotation was taken.

The mathematical formulations in chapter II are insufficiently explained to enable the reviewer to assess their value. They are entirely unconvincing in their present form. However, it seems that no amount of revision or clarification of this or other portions of the book so far discussed will establish the case that the author is attempting to support, unless the conclusions arrived at in chapter VII are sound. In this chapter on "Metals" the author takes upon himself the task of explaining how, for example, iron or nickel catalysts are able to ionize impinging molecules whose ionization potentials are as high as 17 or 18 volts. Final judgment in this connection will have to be left to the mathematical physicist.

P. H. EMMETT.

Hydrophobic Colloids. Symposium on the Dynamics of Hydrophobic Suspensions and Emulsions, held at Utrecht on the 5th and 6th of November, 1937, under the auspices of the Colloidchemistry Section of the Nederlandsche Chemische Vereeniging. 188 pp. Amsterdam: D. B. Centen's Uitg. Mij. N.C., 1938. New York: Nordemann Publishing Co., Inc., 1938. Price: \$2.50.

From a social and propagandistic point of view large scientific gatherings concerned with many fields of work will always be called for. For clearly stating and actually promoting knowledge, meetings of smaller groups of specialists are more important, and they have become therefore more and more popular, for at them it is possible to restrict the number of lectures and to find time for thoroughly discussing the problem in question. An excellent example of this type of meeting is the one in review.

The lectures delivered at the Symposium treated mainly the stability of hydrophobic colloidal solutions and emulsions, the electrical properties of their particles, and the protecting and sensitizing action of hydrophilic colloids. The younger generation of colloidal chemists, more theoretically minded than the older one—Holland may claim to possess a very active and successful group—is right in trying to apply new theoretical conceptions, e.g., Debye-Hueckel's theory, to these problems. The discussion shows that this theory cannot explain in a simple and straightforward way the difficulties of the electrical double layer. Several speakers, representing fairly different points of view, acknowledged that even with poorly hydrated colloids the hydration of the ions, so strongly depending upon their size and charge, is most important and may be decisive for the distribution of the ions on the surface of the particles. This specific nature and hydration of the ions is a cardinal point not covered by Debye-Hueckel's theory. Perhaps the time has come when conceptions concerning hydration, as they are discussed by Bernal and Fowler (*Journal of Chemical Physics*, 1933), may be extended and applied to these colloidal systems.

H. FREUNDLICH.

ELECTROLYTE COAGULATION AND COEFFICIENT OF ELECTROLYTE ACTIVITY¹

WOLFGANG OSTWALD

University of Leipzig, Leipzig, Germany

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I. INTRODUCTION

I believe that a colloid chemist, if asked today to explain the coagulation of a lyophobic hydrosol by electrolytes, will make a rather unhappy face. Most presumably, when explaining simple and well-investigated cases, as, for example, the flocculation of arsenic trisulfide sols with neutral salts, a conscientious colloid chemist will even voice a warning to the effect that this matter is not as simple as it looks.

We can summarize the most important steps in the theory of electrolyte coagulation of feebly solvated sols in abbreviated form by the following headings:

1. Neutralization of charge and equivalent ion exchange.
2. Critical potential.
3. Adsorption as the determining variable of coagulation.
4. The electrokinetic, and not the electrochemical, potential is determinative.
5. Density of charge instead of magnitude of charge.
6. Compression of the double layer.

The sequence of these headings corresponds approximately to the historical development of the theory. We all know that at least the first four assumptions mentioned are wrong. The electrokinetic potential or its reduction is also not determinative for coagulation, as we are finding more and more cases where the rate of electrophoretic migration increases just prior to coagulation (Tuorila, Lagemann, Kruyt and collaborators, Bull and Gortner, Mukherjee, and others). I have nothing to say against the last two assumptions. They may be right; however, they are insufficient. They, too, have so far been unable to give a fairly comprehensive quantitative theory of coagulation. The newest development of the theory, for example, that by the Dutch colleagues (Verwey, Hamaker, etc.), becomes continually more complicated and speculative.

¹ Presented at the Fifteenth Colloid Symposium, held at Cambridge, Massachusetts, June 9-11, 1938.

If a professor is obliged to discuss this unsatisfactory condition of the theory of coagulation for thirty or more years, in every term of the academic year, then it may easily happen that he becomes more and more impatient. Either he becomes resigned or he commences to curse. The latter course is in general more fruitful. Such mental discontent leads one to the experiment of disregarding for the time being the different approaches of the existing theory, or even to forget them entirely, and to consider the possibility of coming closer to the problem in a way entirely *different* from any so far used. Such radical doubts as to the suitability of the theoretical assumptions existing lead, for example, to the following considerations:

A sol is composed not only of a disperse part but also of its dispersion medium. So far, the properties of the disperse part, i.e., of the micelles, have always stood in the foreground of the theory. Their composition, magnitude of charge, their potential, their double layer and its changes, etc., were the center of the theories advanced. The rôle of the dispersion medium was of decidedly less importance. The dispersion medium was considered in the theory primarily as the carrier of the micelles and of the stabilizing and coagulating ions. Possibly the different evaluation of the rôles played by the disperse part and the dispersion medium is incorrect. Possibly we are going a step further when, contrary to prior methods, we put the properties of the dispersion medium in the foreground.

The dispersion medium of a hydrosol is without exception an electrolyte solution both in the condition of stability and in the condition of coagulation. Our concepts of the inner structure of an electrolyte solution are today somewhat at variance with those of the days of van't Hoff and Arrhenius. We assume that such a solution is *a priori* highly dissociated and that the ions in the solution medium are present in a statistic and kinetic type of ionic lattice. In a salt solution there exists, therefore, a certain segregation of the ions. The factor, i , in the concentration equation of van't Hoff and Arrhenius has today been substituted, following the procedure of G. N. Lewis, by the factor f , the coefficient of activity. Instead of referring to the ion concentration ic , we talk about the activity, $fc = a$, where f represents the coefficient of activity. We can either determine f thermodynamically or evaluate the coefficient theoretically, in accordance with the physical theory of Milner-Debye-Hückel. Just as the numerical factor of van't Hoff received the physical significance of the degree of dissociation, we can explain the coefficient of activity from a physical point of view, although it also was first introduced as a numerical factor only. It is a measure of the interionic attraction and therefore of the inner stability of the lattice. These ionic forces will be weaker, the more the value of f in extreme dilutions approaches unity.

From this standpoint a sol exhibits a certain resemblance to a mixed

crystal, but of course only a statistical one. The comparatively giant micelles are built into the highly disperse ionic lattice. If we have a stable sol, the interionic forces will carry these micelles. If the sol is coagulated by dialysis, the interionic forces become too weak to carry the particles any longer. The mutual lattice is torn apart. If the sol coagulates by an increase in electrolyte concentration, a kind of "auto-cleansing" of the statistical ionic lattice takes place. The interionic forces become so large that they drive the micelles together and expel them. It is not the micelles which coagulate owing to mutual attraction; the dispersion medium coagulates the micelles by aggregation and expulsion from the ionic lattice.

This, unquestionably, is a different picture from the usual one. It is now my purpose to demonstrate to you that one can go a step further on this basis than has been done so far, and especially can one actually obtain *quantitative* related functions for coagulation.

II. THE COEFFICIENT OF ACTIVITY

In the following we shall consider only coagulation by typical neutral salts and discard, for example, flocculation by H^+ and OH^- ions or heavy-metal salts. Furthermore, we want to keep in mind that the flocculation values so far have been rather inaccurate data, owing to the difficulty of expressing a time reaction with a single figure. Finally, we shall restrict our discussion to truly lyophobic sols, in which the so-called "ion spreading" between ions of equal valency is experimentally negligible. We shall therefore select a specific type, for example, the negative arsenic trisulfide hydrosol.

According to the briefly sketched idea, it is the coefficient of activity itself and not the activity, the product of f and c , which is determinative. The coefficient of activity referring to *one* ion type, can, according to the physical theory for water at $18^\circ C.$, be defined as

$$-\log f^+ = 0.5z_+^2 \sqrt{u}$$

where z represents the valency and u the ionic strength. $u = 1/2(m_+ \cdot z_+^2 + m_- \cdot z_-^2)$, where m_+ = molality of the cation, z_+ the valency of the cation, m_- the molality of the anion, and z_- the valency of the anion. Both ions are therefore taken into consideration. The value of f^+ varies greatly with the value of both ions and with concentration, as can be seen in table 1.

In the first column the type of salt is given, in the second the value for the molality of the salt solution, which corresponds to a *constant* value for $f^+ = 0.70$. We find that, depending on the structure and the valence of the ions, the coefficient of activity of very different concentrations (molalities) corresponds to the same value for f^+ , i.e., the same intensity of

interionic forces. The relative figures in the last column will remind a colloid chemist vividly of the relative coagulation values for salts of different valencies. In these cases too, as is known, one needs decidedly smaller concentrations of polyvalent cations for coagulation, and here, too, the

TYPE OF SALT*	MOLALITY (<i>m</i>) AT $f^+ = 0.70$	<i>m</i> (RELATIVE)
+ -		
1 - 1	0.096	100,000
1 ₂ - 2	0.068	70,800
1 ₃ - 3	0.050	52,000
1 ₄ - 4	0.042	43,800
2 - 1 ₂	0.0022	2,290
2 - 2	0.0017	1,770
3 - 1 ₃	0.00022	229
3 ₂ - 2 ₃	0.00017	177
3 - 3	0.000145	151
4 - 1 ₄	0.000040	42
6 - 1 ₆	0.000004	4

* The subscripts represent the number of ions present in a molecule.

TABLE 2
Arsenic trisulfide sols
(H. Schulze: J. prakt. Chem. 25, 431 (1882))

TYPE OF SALT	NUMBER OF SALTS	<i>m</i> ₂ (MEAN VALUE)	f^+	f^+
1 - 1	11	0.109	0.69	0.69
1 ₂ - 2	5	0.0578	0.71	0.51
1 ₃ - 3	1	0.0375	0.73	0.39
1 ₄ - 4	1	0.0405	0.69	0.23
2 - 1 ₂	5	0.00172	0.72	0.85
2 - 2	6	0.00246(!)	0.63*	0.63
3 - 1 ₃	3	0.000176	0.72	0.89
3 ₂ - 2 ₃	1	0.000112	0.74	0.81

Mean value of f^+ (with *) = 0.71 ± 0.03 (about 4 per cent).

Mean value of f^+ (without *) = 0.70 ± 0.55 (about 8 per cent).

counter ions of the same valence have a certain, although decidedly smaller, influence on the coagulation value.

I have checked many hundreds of coagulation values to see whether there exists a quantitative relation between coefficient of activity and coagulation value. Tables 2, 3, 4, 5 and 6 give a few examples thereof.

In these tables m_k represents the coagulating molality. To eliminate the influence of the cation spreading, only the mean values for m_k of one valency class of ions were used in the calculation. Where more than one

TABLE 3
Arsenic trisulfide sols

TYPE OF SALT	NUMBER OF SALTS	m_k (MEAN VALUE)	f^+
(S. E. Linder and H. Picton: J. Chem. Soc. 67, 63 (1895))			
1 - 1	13	0.0954	0.70
1 ₂ - 2	4	0.0316	0.78
2 - 1 ₂	21	0.00128	0.75
2 - 2	7	0.00186(!)	0.67*
3 - 1 ₂	2	0.000099	0.78
3 ₂ - 2 ₃	6	0.000112	0.74
(H. Freundlich: Z. physik. Chem. 44, 135 (1903))			
1 - 1	5	0.0502	0.77
1 ₂ - 2	1	0.0164	0.83
2 - 1 ₂	1	0.000672	0.82
2 - 2	7	0.000810	0.77
3 - 1 ₂	2	0.000093	0.78
3 ₂ - 2 ₃	1	0.000046	0.82

Mean value of $f^+ = 0.80 \pm 0.03$ (3.8 per cent).

TABLE 4
Antimony trisulfide sols

TYPE OF SALT	NUMBER OF SALTS	m_k (MEAN VALUE)	f^+
(H. Schulze: J. prakt. Chem. 27, 328 (1883))			
1 - 1	2	0.129	0.66
1 ₂ - 2	2	0.0732	0.68
2 - 1 ₂	4	0.00216	0.69
2 - 2	2	0.00402(!)	0.63(!)
3 - 1 ₂	1	0.000247	0.67
(A. Iwanitzkaja-Orlowa: Kolloid-Beihefte 18, 1 (1923))			
1 - 1	3	0.0293	0.82
2 - 1 ₂ (chlorides)	4	0.000362	0.86
2 - 1 ₂ (nitrates)	4	0.000475	0.84
3 - 1 ₂	3	0.000023	0.88

ion is present in the molecule, as, for example, in potassium sulfate, the molar coagulation concentration only refers as usual to one cation (= $1/2 K_2SO_4$).

The tables, which could be increased in number by dozens, demonstrate that the coefficient of activity actually represents approximately the measure for the flocculation power of neutral salts in hydrophobic sols. *Electrolyte-containing dispersion media will flocculate at approximately the same value for the coefficient of activity of the dominating ions.* This is the first quantitative consequence of this new method of consideration.

TABLE 5
Influence of counter ions on arsenic trisulfide sols
(Wo. Pauli and E. Valkó)

AUTHOR	CONCENTRATION OF SOL IN GRAMS PER LITER	SALT	FORMULA WEIGHT IN EQUIVALENT MILLIMOLES PER LITER	m_k	f^+
Freundlich.....	1.8	KCl	49.5	0.0495	0.774
		K ₂ SO ₄	65.5	0.0328	0.774
		K ₄ Fe(CN) ₆			
Ghosh and Dhar.....	3.7	KCl	85	0.085	0.72
		K ₂ SO ₄	100	0.050	0.73
		K ₄ Fe(CN) ₆	185	0.046	0.68
Weiser and Nicholas.....	6.0	KCl	33.2	0.0332	0.811
		K ₂ SO ₄	43.5	0.0218	0.812
		K ₄ Fe(CN) ₆	71.2	0.0178	0.791

TABLE 6
Ferric oxide sols

TYPE OF SALT	NUMBER OF SALTS	m_k (MEAN VALUE)	f^- (POSITIVE SOL)
(H. Freundlich: Z. physik. Chem. 44 , 135 (1903))			
1 - 1	5	0.01175	0.88
1 ₂ - 2	4	0.000296	0.87
2 - 2	2	0.00021	0.88
(H. Freundlich, Joachimsohn, and Ettisch: Z. physik. Chem. 141 , 249 (1929))			
1 - 1	1	0.013	0.88
1 ₂ - 2	1	0.00039	0.86
1 ₃ - 3	1	0.000031	0.87
1 ₄ - 4	1	0.000015	0.80

III. QUANTITATIVE RELATION BETWEEN COAGULATION VALUE AND VALENCE

If this relation stands, then automatically, or better, mathematically, a new quantitative formulation of the Schulze-Hardy valence rule results. The former mathematical formulations of this rule, as, for example, those of Whetham, Robertson, and also myself have already been found in-

sufficient, for the reason that they did not consider the influence of the equally charged counter ions. From the relation $f_k^+ = \text{constant}$ and the equation defining the coefficient of activity, we now obtain for the molecular flocculation power ($1/m_k$) the relation:

$$\frac{1}{m_k} = \frac{z_+^5(z_+ + z_-)}{2K}$$

TABLE 7
Arsenic trisulfide sols

TYPE OF SALT	$1/m \cdot n_+$ (RELATIVE)	$1/m \cdot n_+$ (MEAN VALUE; EXPERIMENTAL)
1 - 1	1	1
1 ₂ - 2	1.5	1.65
1 ₃ - 3	2.0	2.5
1 ₄ - 4	2.5	2.8
2 - 1 ₂	48	51
2 - 2	64	+47
3 - 1 ₃	486	573
3 ₂ - 2 ₃	608	938
4 - 1 ₄	2,560	1,720
6 - 1 ₆	27,216	14,050

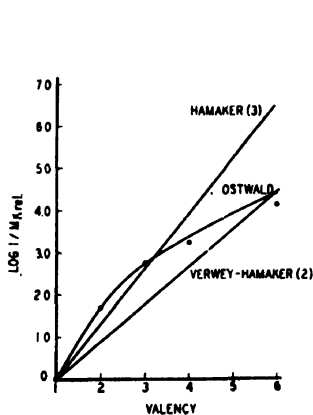


FIG. 1

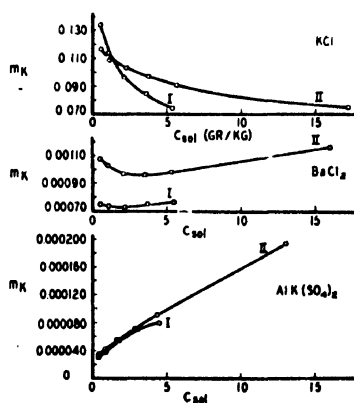


FIG. 2

FIG. 1. Relation between coagulation value and valence

FIG. 2. Effect of concentration of sol on the coagulation value.

/ Here we only have one constant which is characteristic for the sol, whereas the numerical factor $2 = 1/0.50$, the characteristic constant of the coefficient of activity equation for water at 18°C., is independent of the

sol. We find that in this equation the valence of the counter ions is also considered.

Table 7 shows how closely the new formulation of the Schulze-Hardy rule corresponds to experiment. Mean values taken from the above tables on measurements of arsenic trisulfide sols have been used.

Recently, Verwey and Hamaker have also evaluated quantitative relations between coagulation value and valence, but in rather speculative ways. These results are graphically demonstrated in figure 1. The valence is given on the abscissa and on the ordinate the logarithm of $1/m_k$. The circles represent the experimental mean values of table 7 taken from work on arsenic trisulfide sols. One realizes that the relations as postulated by Verwey and Hamaker are principally in error, notwithstanding the many assumptions which had to be made *ad hoc*. The relation between the logarithm of the coagulating power and the valence cannot be represented by a straight line, as was done by Verwey and Hamaker, but only by a curved one, as it results directly, for example, from the theory of the coefficient of activity.

IV. THE EFFECT OF SOL CONCENTRATION ON THE COAGULATION VALUE

It is known that the concentration of the sol (C_{sol}) influences the coagulation value, and, according to the valence of the dominant ion, frequently in a different way. The most important case, the basis for the so-called Burton's rule, can be demonstrated by figure 2.

When dealing with a monovalent cation, the coagulation molality decreases with increasing sol concentration; in the case of trivalent or higher valent cations, it increases. Weiser and others have demonstrated that exceptions to this course are known, as, for example, with chromic hydroxide and ferric hydroxide sols. I do not intend to discuss in this paper the theory of these relations and should like to refer to a paper published elsewhere.² From an experimental point of view it should be pointed out that, according to recent investigations in my laboratory undertaken at extreme dilutions of the sols, all curves bend upward. In the case of infinitely dilute sols, one would therefore need infinitely concentrated salt solutions to obtain coagulation, an unquestionably obvious conclusion.

How will these curves look if we plot the coefficient of activity at the coagulation point against the sol concentration, instead of the coagulation molalities? Figure 3 gives a picture of this new method of graphical representation. First of all, we can place all curves in one coordinate system, and all curves approach each other with increasing sol concentration. Figures 4 and 5 give further examples.

We find that with increasing sol concentration the curves approach a

² Kolloid-Z. 80, 304 (1937).

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common point. The rule that the coefficient of activity is a constant in the case of coagulation will be more exact the more concentrated the sol. As a result of very recent investigations, which have been undertaken with a

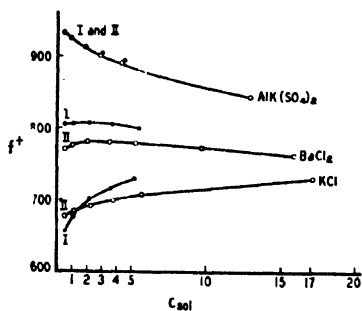


FIG. 3

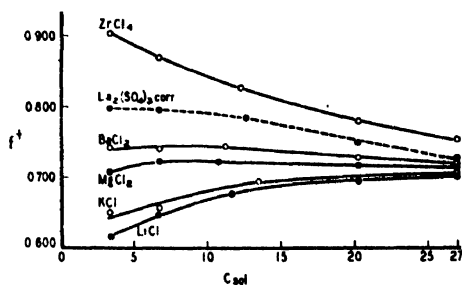


FIG. 4

FIG. 3. Plot of coefficient of activity at the coagulation point against sol concentration.

FIG. 4. Plot of coefficient of activity at the coagulation point against sol concentration.

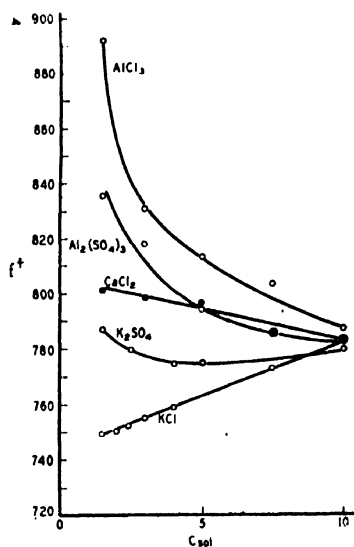


FIG. 5

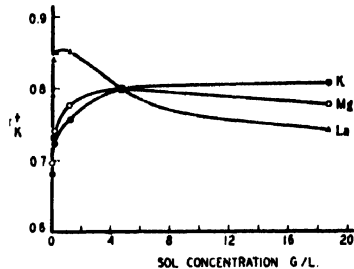


FIG. 6

FIG. 5. Plot of coefficient of activity at the coagulation point against sol concentration.

FIG. 6. Plot of coefficient of activity at the coagulation point against sol concentration for arsenic trisulfide sols. Appearance of "over optimal" sol concentration.

special technique for determining coagulation points, there seemed to exist "over optimal" sol concentrations, as is demonstrated in figure 6, using arsenic trisulfide sols. Admittedly, so far only one single case of this type

has been found, so that it is premature to decide whether such an intersecting of the curves is a general rule.

V. PHENOMENON OF DOUBLE COAGULATION

Every colloid chemist is familiar with the phenomenon of double coagulation, or the so-called "irregular series" of coagulation. Table 8 represents a common example of a mastic sol. If one successively increases the concentration of a salt with polyvalent cations (negative sols), one obtains two zones of coagulation and three coagulation values: f_{k1} , f_{k2} , and f_{k3} . If one considers that every hydrosol needs a minimum ion concentration for

TABLE 8

Coagulation values obtained in treating a gum mastic sol, concentration 0.688 g. per liter, with aluminum chloride
(Boutaric)

COAGULATION VALUES		
0.000040	Stable	
0.000067	Stable	$f_{k1}^+ = 0.936$
0.000075	Coagulated in 3 min.	0.933
0.000100	Coagulated instantly	0.923
0.000125	Coagulated in 1 min.	
0.000250	Coagulated in 5 min.	
0.000300	Coagulated in 2 hr.	$f_{k2}^- = 0.995$
0.000400	Stable	0.994
0.000750	Stable	
0.00150	Coagulated in 2 hr.	
0.00310	Coagulated in 10 min.	
0.00620	Coagulated in 2 min.	$f_{k3}^- = 0.960$
0.0125	Coagulated instantly	0.944
0.0500	Coagulated instantly	
0.0200	Coagulated instantly	
0.0750	Coagulated instantly	

its stability which cannot be reduced below a certain value without coagulation by dialysis, then we have a fourth value of coagulation, f_{k0} , whose molality is very low, or, in other words, whose coefficient of activity must be close to unity. This double coagulation is, as known, caused by reversal of charge of the sol, owing to a higher concentration of polyvalent ions.

To the best of my knowledge, no one has ever brought up the question whether these four different molalities of coagulation happen to be related to each other in some quantitative way. Let us consider figure 7 for this purpose. As abscissa we have plotted the logarithm of molality, as ordinate the two individual coefficients of activity, f^+ and f^- . We have

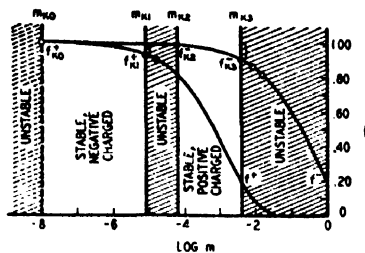


FIG. 7

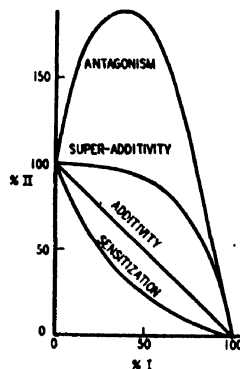


FIG. 8

FIG. 7. Plot of log of molality against f^+ and f^-

FIG. 8. Coagulation by salt mixtures

TABLE 9
Coagulation of a gum mastic sol
(Buxton, Teague, and Shaffer)

m_i	RESULTS	
FeCl_3		
0.0000208	No coagulation	
0.0000557	No coagulation	
0.0000833	Coagulation	$f_{k1}^+ = 0.79; f_{k2}^- = 0.985$
0.000163	No coagulation	
0.0333	Coagulation	$f_{k3}^- = 0.74$
$\text{Fe}(\text{NO}_3)_3$		
0.0000333	No coagulation	
0.0000557	Coagulation	$f_{k1}^+ = 0.83$
0.0000833	Coagulation	$f_{k2}^- = 0.985$
0.000166	No coagulation	
0.00833	Coagulation	$f_{k3}^- = 0.86$
AlCl_3		
0.0000833	No coagulation	
0.000166	Coagulation	$f_{k1}^+ = 0.72$
0.000333	Coagulation	$f_{k2}^- = 0.971$
0.000666	No coagulation	
0.0333	No coagulation	(0.74)
0.0833	Coagulation	$f_{k3}^- = 0.63$

two zones of stability and three zones of instability. The two *S*-curves demonstrate the changes of the two coefficients of activity with the logarithm of concentration. Let us consider the points where the *S*-curves intersect with the stability zones. We find that always two coagulation points belong together: f_{k0} and f_{k2} on one hand, and f_{k1} and f_{k3} on the other hand. Two of these points lie at the same height. That means nothing else but that at double coagulation the four coagulation values are quan-

TABLE 10
Formol gold, undialyzed, treated with aluminum chloride
(Fuchs and Pauli: Kolloid-Beihefte 21, 412 (1925))

<i>m</i>	RESULT AFTER 24 HR.	
0.00002	No noticeable change	
0.00006	Violet, not completely coagulated } Coagulated }	$f_{k1}^+ = 0.822$
0.00007		$m_{k1} = 0.809$
0.00008		$= 0.797$
0.0003	Red-violet color	$m_{k2} \quad f_{k1}^- = 0.972$
to	to	
0.002	Red color	
0.003	Red	
0.018	Blue, coagulated	$m_{k3} \quad f_{k3}^- = 0.804$

$$-\log f^+ = 4.5\sqrt{6m}; \quad -\log f^- = 0.5\sqrt{2m}$$

TABLE 11
Formol gold sol
(Boutaric and Dupin)

SALT	m_{k1}	f_{k1}^+	m_{k2}	f_{k2}^-	m_{k3}	f_{k3}^-
AlCl ₃	0.00000319	0.956	0.00026	0.977	0.00095	0.951
ThCl ₄	0.00000758	0.956	0.000444	0.962	0.000823	0.949
FeCl ₃	0.00000146	0.911	0.000243	0.975	0.001625	0.937

titatively related to each other. *The value of the positive coefficient of activity at the coagulation point of a negative sol equals the value of the negative coefficient of activity at the point of coagulation of the charge-reversed positive sol, etc.*

The last two figures have demonstrated that this coefficient of activity rule is supported by facts. The examples in tables 9, 10, and 11 might further substantiate this.

To be able to test the equality of f_{k0} and f_{k2} more accurate data in regard

to the electrolyte content at dialytic flocculation are needed. From the available experimental values for f_{12} one can deduce that these dialytic coagulation values must be, in full accord with experience, extremely small.

VI. COAGULATION BY SALT MIXTURES

A group of the most peculiar phenomena are found in the coagulation by salt mixtures. We place the coagulation value of a monovalent salt at 100 and also the coagulation value of a single trivalent salt. If we now examine the coagulating power of mixtures of these two salts we very rarely obtain additivity. As figure 8 demonstrates, we find either sensitization, super-additivity, or antagonism. This latter effect is particularly striking. The coagulation molality of the mixtures can be many hundreds above the 100 per cent for the individual values. The reason for this anomaly is not yet clear. Might it be possible that the proposed theory would also give us some new ideas as to these phenomena?

Naturally one can also evaluate the coefficient of activity of salt mixtures. I am refraining from reproducing here the somewhat cumbersome formulas and prefer simply to give some actual examples. If we look at a mixture of equimolal solutions, we have, for example:

$$0.001 \text{ } m \text{ KCl; } I f^+ = 0.964$$

$$0.001 \text{ } m \text{ AlCl}_3; II f^+ = 0.449$$

$$0.001 \text{ } m \text{ KCl} + 0.001 \text{ } m \text{ AlCl}_3; I + II f^+ = 0.709$$

The coefficient of activity of the mixture therefore lies *between* the values for the individual coefficients.

If we now look at a mixture of both salts, of *unequal* molality but of *equal coefficient of activity*, we obtain the following figures:

$$0.0612 \text{ } m \text{ KCl; } I f^+ = 0.750$$

$$0.000126 \text{ } m \text{ AlCl}_3; II f^+ = 0.750$$

$$0.0612 \text{ } m \text{ KCl} + 0.000126 \text{ } m \text{ AlCl}_3; I + II f^+ = 0.914$$

In such a mixture we obtain a material increase of the joint coefficient of activity. According to the first-mentioned coefficient of activity rule, this means that when using such mixtures a much higher molality is necessary for coagulation than would correspond to additivity. The appearance of ion antagonism in such coagulation experiments is also contained in the new theory.

Figure 9 gives only one example from a large number of theoretical calculations available, namely, the combination of a monovalent salt with a polyvalent one. We can see that the antagonism becomes more pronounced the larger the valence difference between the two salts. In a

mixture of two salts of the same valence no antagonism exists. These, as well as further theoretical postulates, are in full accord with experiment. Figures 10 and 11 give two examples of the attempt to evaluate experimental cases quantitatively by the new theory. That we have not obtained better agreement is due to the fact that the sols were too dilute, so that the first coefficient of activity rule could not be exactly fulfilled. Compare, for example, the differences in the f_k values in figure 10. Furthermore, the location as well as the height of the maximum are extremely sensitive towards minute variations of the proportions in the mixture.

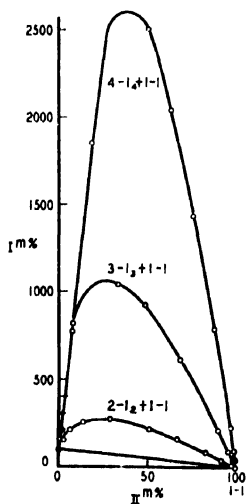


FIG. 9

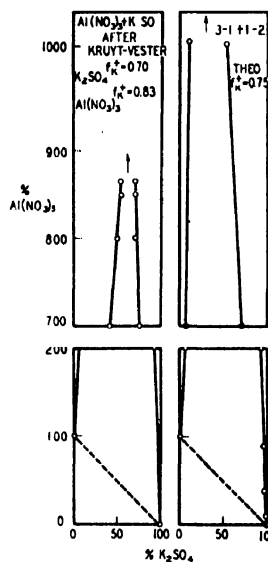


FIG. 10

FIG. 9. Coagulation by a monovalent salt combined with a polyvalent one.

FIG. 10. An example of the attempt to evaluate experimental cases quantitatively by the new theory.

Experimental errors in the fifth decimal point of the molality are clearly noticeable in the curves.

VII. THE EFFECT OF CHANGES IN SOLVENT AND TEMPERATURE

The equation defining the coefficient of activity as given above holds only for water at 18°C. If we change the nature of the solvent, for example, by the addition of alcohol or, if we coagulate at other temperatures, we must apply the extended equation for f^+ which is given by:

$$-\log f^+ = \frac{0.434e^2}{2DkT} \sqrt{\frac{1}{DT}} \cdot z_+^2 \sqrt{\frac{1}{2} \sum m \cdot z^2}$$

where e = elementary electric charge, D = dielectric constant, T = absolute temperature, k = Boltzmann's constant, and the root content = ionic strength. As can be seen, the coefficient of activity is a multi-function of the dielectric constant and temperature. It may not be overlooked that D in itself already is a function of T .

If the proposed theory is correct, the coagulation molalities in the cases discussed must decrease with increasing temperature as well as with increasing addition of a solvent with lower D , for example, alcohol. Figure 12 reveals the decrease of m_k for the case in which f^+ , the coefficient of activity at the point of coagulation, equals 0.75. This means that by the addition of ethanol the coagulation value can be reduced much more easily and much more markedly than by an increase in temperature. The curvature of the two curves is opposite.

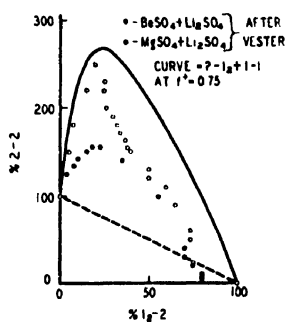


FIG. 11

FIG. 11. Another example of the attempt to evaluate experimental cases quantitatively by the new theory.

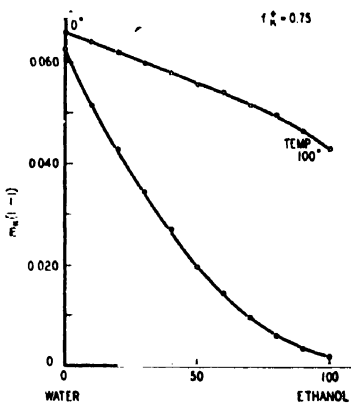


FIG. 12

FIG. 12. Effect of ethanol and of temperature upon the coagulation of arsenic trisulfide sols by salts.

If this deduction is tested experimentally, one actually obtains (with normal and neutral salts) these two types of curves, as shown in figures 13 and 14, resulting from my own measurements on arsenic trisulfide sols.

Naturally one can also start with an ethanol or propanol sol, as, for example, Weiser and Mack (8) did, and change D by the addition of water, as can be seen on the right-hand side of figure 14. One obtains the same curves.

The theory also permits one to predict the magnitude of such a variation for the coagulation value when varying the temperature and the D of the solvent. For this purpose it is only necessary to introduce into the above

formula, which contains D and T , the new values of D and T . Instead of the numerical factor 0.505 we will obtain other numerical factors. If the theory is correct the f_h^+ values must remain constant, notwithstanding variations in temperature and the nature of the solvent.

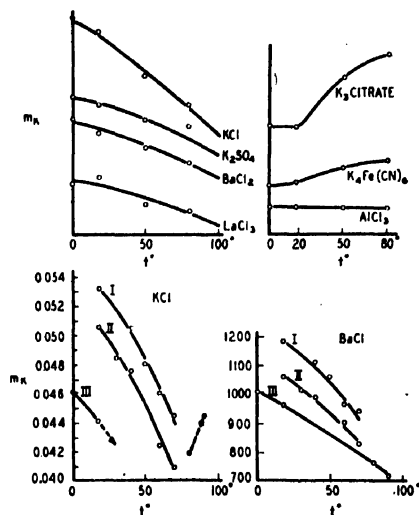


FIG. 13. Effect of temperature on the coagulation of arsenic trisulfide sols by salts

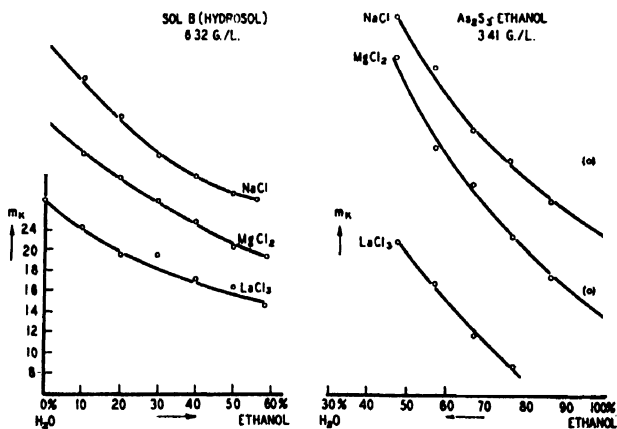


FIG. 14. Effect of ethanol on the coagulation of arsenic trisulfide sols by salts

Table 12 shows some figures taken from measurements on arsenic trisulfide sol. The measurements are not simple to perform, because, especially at higher temperatures, the sols themselves hydrolyze and it is therefore necessary to work very fast. However, the constancy of f_h^+ is, on the average, to be considered as very good.

The last tables, tables 13 to 16, show similar quantitative tests with changes of the dispersion medium. Table 13 refers to measurements by C. H. Sorum (5) on ferric oxide sols up to very high concentrations of

TABLE 12
Arsenic trisulfide sol B; f_{\pm}^{\dagger} values at varying temperatures

SALT	0°C.	18°C.	30°C.	40°C.	50°C.	60°C.	70°C.	80°C.	90°C.	MEAN VALUE
KCl I		0.766		0.764	0.765	0.766	0.765			0.765
KCl II		0.772	0.772	0.770	(0.779)	0.775	0.774			0.773
KCl III	0.786	0.785						(0.767)	(0.755)	(0.776)
K ₂ SO ₄ I		0.783	0.784	0.783	0.783	0.780	0.776			0.781
K ₂ SO ₄ II	0.798							(0.767)	(0.755)	(0.773)
BaCl ₂ I		0.761		0.762	0.763	0.764	0.764			0.763
BaCl ₂ II		0.771	0.776	0.770	(0.779)	0.773	0.777			0.773
BaCl ₂ III	0.785	0.780						0.780	0.780	0.781

TABLE 13
*Experiments on ferric oxide sol
(C. H. Sorum)*

SOL	ETHANOL	D	φ_D	m_{\pm} FOR NaCl	f_{\pm}^{\dagger}
	<i>per cent</i>				
IIIa; 2.0 g. Fe ₂ O ₃ per liter	0	80.4	0.500	0.022	0.84
	10.2	74.5	0.561	0.016	0.85
	20.4	68.7	0.632	0.012	0.85
	43.1	54.0	0.909	0.008	0.83
	54.9	47.4	1.102	0.007	0.81
IIIb; 4.0 g. Fe ₂ O ₃ per liter	0	80.4	0.500	0.014	0.87
	10	74.6	0.562	0.011	0.87
	20	68.9	0.623	0.010	0.87
	40	56.1	0.857	0.008	0.84
	45	53.0	0.935	0.007	0.835
IIIc; 8.0 g. Fe ₂ O ₃ per liter	0	80.4	0.500	0.014	0.87
	10	74.6	0.562	0.008	0.88
	20	68.9	0.623	0.007	0.89
	40	56.1	0.857	0.007	0.85
	45	53.0	0.935	0.006	0.85

alcohol. Table 14 shows propanol sols of mercuric sulfide, studied by Weiser and Mack (8), to which water had been added. Table 15 refers to my own measurements on arsenic trisulfide hydrosols. The constancy of

TABLE 14
Mercuric sulfide-propanol sols
 (H. B. Weiser and G. L. Mack)

PER CENT H ₂ O	D^*	PER CENT H ₂ O	D	$\varphi_D \cdot \frac{1}{z+1}$	m_k	D_k^{f+}
0	22.0	LiCl				
5	23.25	0	22.0	3.50	0.0033	0.63
10	24.5	5	23.25	3.25	0.0037	0.63
15	27.1	15	27.1	2.56	0.0043	0.68
20	29.8	22	30.3	2.11	0.0064	0.68
25	32.4	25	32.4	1.96	0.0092	0.65
30	35.5	CaCl ₂				
35	38.5	0	22.0	24.3	0.0544	0.89
40	41.5	5	23.25	22.5	0.0570	0.87
45	45.0	10	24.5	20.6	0.04119	0.85
		15	27.1	17.75	0.0419	0.84
		20	29.8	15.3	0.0431	0.82
		25	32.4	13.6	0.052	0.80
		30	35.5	11.85	0.0482	0.78
		35	38.5	10.9	0.0513	0.75
		40	41.5	9.35	0.05235	0.74
		45	45.0	8.28	0.05335	0.71

* Own measurements.

TABLE 15
Influence of ethanol on coagulation of arsenic trisulfide hydrosols

ETHANOL	NaCl		MgCl ₂		LaCl ₃	
	m_k	D_k^{f+}	m_k	D_k^{f+}	m_k	D_k^{f+}
Sol A: 0.50 g. per liter						
per cent						
0	0.046	0.779	0.0575	0.802	0.050	0.836
10	0.038	0.791	0.0550	0.820	0.040	0.837
20	0.032	0.779	0.0550	0.805	0.033	0.838
30	0.0254	0.780	0.0545	0.795	0.031	0.826
40	0.0192	0.783	0.05325	0.802	(0.031)	(0.801)
46.6	0.017	0.777				
47.6					(0.031)	(0.786)
50				0.798		
Sol B: 2.53 g. per liter						
0	0.0608	0.751	0.0590	0.785	0.050	0.784
10	0.0517	0.748	0.0574	0.786	0.076	0.786
20	0.0419	0.751	0.062	0.786	0.062	0.785
30	0.0321	0.756	0.0550	0.785	(0.062)	(0.763)
40	0.0263	0.751	0.0539	0.785	(0.050)	(0.755)
50	0.0220	0.736	0.0528	0.787	(0.046)	(0.733)
56	0.0203	0.738				
57.38			0.0522	0.786		
58					(0.036)	(0.737)

f_k^+ is unexpectedly good. Only the trivalent lanthanum chloride does not conform to the rule at higher alcohol concentrations. Table 16 demonstrates the influence of water on an ethanol sol. If one compares the figures in table 16 in horizontal order one again obtains an example for the correctness of the basic coefficient of activity rule (Ak — rule): f_k is approximately constant even if the valence of the coagulating salt is varied.

TABLE 16

Influence of water on coagulation of arsenic trisulfide-ethanol sols

Sol contains 1.7 g. arsenic trisulfide per liter

WATER	NaCl		MgCl ₂		LaCl ₃	
	m_k	Df_k^+	m_k	Df_k^+	m_k	Df_k^+
<i>per cent</i>						
96	0.0045	0.796	0.0425	0.813	(0.0414)	(0.610)
86.4	0.0025	0.803	0.0375	0.806	(0.0412)	(0.720)
76.8	0.0045	0.795	0.0475	0.814	0.049	0.797
67.2	0.0060	0.806	0.05125	0.806	0.047	0.808
57.6	0.0090	0.802	0.05163	0.813	0.047	0.809
48.0	0.0115	0.794	0.05250	0.802	0.0423	0.808

VIII. SUMMARY

Summing up, the tables and curves as given seem to demonstrate that the new idea proposed herein, namely, to place the properties of the dispersion medium in the focal point of the theory, is rather fruitful. Seemingly, the quantitative characteristics of the electrolytic dispersion medium and the coefficient of activity offer a tool which permits a quantitative control of a number of coagulation phenomena.

Let us return to our original question: What actually happens during the coagulation of a hydrophobic sol by neutral salts? We now might formulate the following reply: The coagulating forces seem to be the same as the interionic attraction forces between ions of the dispersion medium. This results from the fact that the coefficient of activity, the measure for these forces, also plays a predominant rôle in coagulation. Nevertheless, it might be wise to add that the entire mechanism even today is not as simple as the procedure actually looks.

The new theory is by no means contrary to the many attempts to evaluate the rôle played by the double layer between the disperse part and the dispersion medium. The only difference is that now the double layer is looked upon as an interposed apparatus of the dispersion medium, and not as the coagulating motor itself. The dispersion medium brings about coagulation and not the double layer. It is the arm that hits and not the cane.

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BOUNDARY TENSION BY PENDANT DROPS¹

J. M. ANDREAS, E. A. HAUSER, AND W. B. TUCKER

*Department of Chemical Engineering, Massachusetts Institute of Technology,
Cambridge, Massachusetts*

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Boundary tension is a measure of the free energy of a fluid interface. The term is derived from the superficial analogy between the surface of a liquid and a stretched membrane. For, just as it has proven to be convenient to express the potential energy of a fluid mass in foot pounds per pound as a "head" in feet, it has been shown to be useful to speak of the free energy of a fluid surface in ergs per square centimeter as a "tension" in dynes per centimeter.

Surface tension is the boundary tension at an interface between a liquid and a gas or vapor, and interfacial tension is the boundary tension at a phase boundary between two incompletely miscible liquids.

Nearly all of the common specific properties of fluids, such as the density, boiling and freezing points, optical rotation, and thermal conductivity, are properties of the main body of the fluid. The boundary tension is the best known property of liquid *surfaces*. For this reason it is of outstanding importance in colloid chemistry, which frequently is called the chemistry and physics of surfaces and surface reactions. The usefulness of boundary tension measurements has been limited in the past by the great difficulty of making determinations with satisfactory speed, accuracy, and precision.

A great many procedures have been developed for the determination of boundary tension, of which the majority are just barely workable and are characterized by low precision and lack of versatility. Of seventeen methods listed by N. E. Dorsey (6) in 1926, only a few are in common use. These depend upon observing: (a) the behavior of a liquid in a capillary tube (24, 35, 46); (b) the force required to pull a wire ring or staple out of the liquid surface (29, 36); (c) the weight or volume of drops falling from a vertical tube of known size (15, 16); or (d) the maximum pressure required to form bubbles in a liquid from a tube of known size (47, 53). Each of these methods has serious limitations (1).

This lack of a generally satisfactory method of measurement suggested that it would be profitable to resurvey the field in search of some possi-

¹ Presented at the Fifteenth Colloid Symposium, held at Cambridge, Massachusetts, June 9-11, 1938.

bility which had been overlooked by the earlier workers and in the hope that a new method could be developed which would succeed where others had failed.

Previous work (8) had demonstrated that the method of pendant drops has a number of outstanding advantages over other methods. Outstanding from the colloid chemist's point of view is the fact that this method is a static one. Once the surface is formed, it is not subjected to any changes due to outside influence prior to or during the measurement. It is the only known method which permits an accurate study of changes in surface composition with time, a phenomenon of predominant importance in the study of various colloidal systems. Accordingly, the focus of our attention was on the design of apparatus and the development of methods with which its possibilities could be explored. In addition to this, an extensive series of measurements was made of typical liquid systems to show the range of usefulness of the new method and to show the sort of results which can be expected.

The method which was decided upon consists in suspending a small drop of the liquid to be tested from the end of a vertical tube which is mounted in a thermostat. The surface of the drop will be a surface of revolution whose shape and size can be determined by measurements made on a large photographic image obtained with a special camera built for the purpose. Since the equations determining the equilibrium of the drop are known, the boundary tension of the liquid can be calculated from a few simple measurements made on a photograph of a hanging drop.

This method has been undeservedly in disrepute for a number of years, because the first workers (11, 55) who attempted to employ it had no satisfactory pendant drop camera and used methods of calculation which were tedious and of low precision. These difficulties have now been overcome.

APPARATUS

The apparatus consists, essentially, of a light-source, a thermostat chamber, a set of drop-forming tips, and a precise camera having a fixed image distance and a telecentric lens system (figure 1).

Experience shows that monochromatic light gives slightly more satisfactory images than white light. It can conveniently be obtained by using a mercury arc lamp (GE, Type H-3, 85-watt, high pressure) and gelatin filter (Wratten No. 77-A) combination.

The drop hangs from a vertical, cylindrical tip in a glass cuvette inside the thermostat (figure 2). In this way the drop is maintained at all times in physical equilibrium with its surroundings. The inner chamber of the thermostat must be totally enclosed to prevent loss of liquid by evaporation, and it should be held to within $\pm 0.05^\circ \text{C.}$ of the desired temperature, since solubilities, vapor pressures, and boundary tensions all change with

temperature. Our thermostat was maintained to within $\pm 0.01^\circ \text{C}$. by a sensitive thermoregulator.

To guarantee such constant temperatures, water from a tank containing the thermoregulator was pumped through the thermostat at a rate of 30 gallons per minute. Vibrations set up by the pump were absorbed by

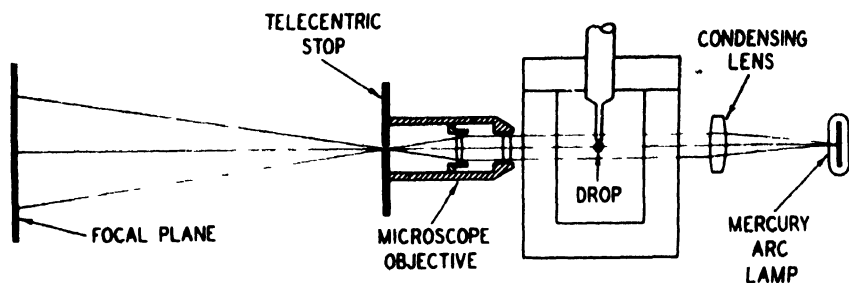


FIG. 1 The apparatus

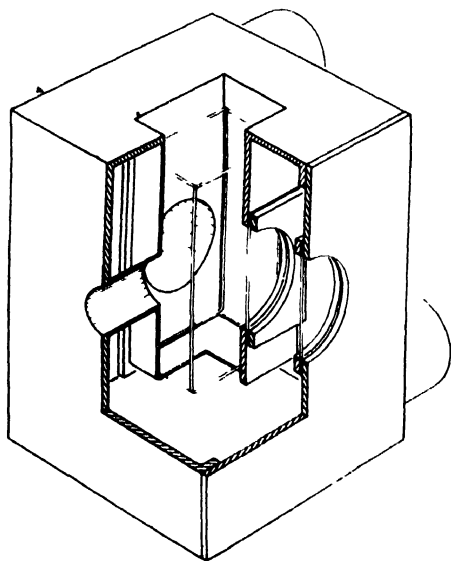


FIG. 2

FIG. 2. Thermostat containing cuvette

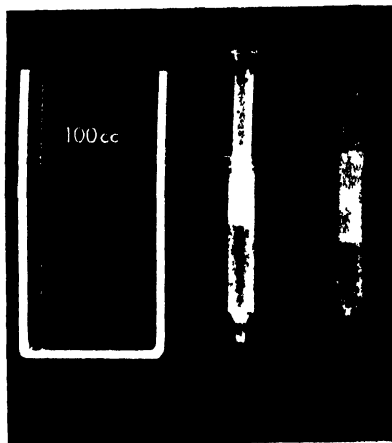


FIG. 3

FIG. 3. Cuvette and drop-forming tip prepared from hypodermic syringe

flexible rubber hose connections between pump and thermostat. The thermostat was chromium-plated to minimize radiant heat transfer.

Drop-forming tips for surface tension measurements can conveniently be made by welding short lengths of 2-mm. Pyrex tubing on standard 1.5-cc. hypodermic syringes (figure 3). It is desirable that the end of the tip be made from tubing having a circular cross section, and that the end be cut off perpendicular to the vertical axis. However, microscopic perfec-

tion is not essential, since the liquid surface tends to bridge over any minor irregularities. The measurements are made at points on the liquid surface which are remote from the end of the tip and where the influence of imperfections in the shape of the tip is normally negligible. Interfacial tension measurements require a set of tips of various diameters if the drops are always to have a convenient shape. Diameters ranging from 0.2 to 20.0 mm. may be required in exceptional cases. Rectangular cuvettes built of optically flat glass can be purchased from dealers in scientific apparatus.

The construction of a satisfactory camera is a matter of considerable experimental difficulty and determines to a large extent the success of the final results. The exact details of the design depend upon the method by which the image is to be measured and upon the precision which is required, but certain features must be incorporated in any case. It is essential for the drop to be photographed with rays of light which are parallel to the optical axis, if error due to perspective is to be avoided. We accomplished this by using standard microscope objectives of 48 or 24 mm. focal lengths which were equipped with telecentric stops. The camera should be built to make pictures on glass plates and to have an optical magnification of from 10 to 30 diameters.

CALCULATIONS

A. The method of the plane of inflection

The boundary tension can be computed directly from an analysis of the stresses in a static, pendant drop. The mathematical treatment is based on two fundamental equations. The first of these states that the pressure caused by the curvature of the surface is equal to the product of the boundary tension and the mean curvature.² The second says that, when the drop is in equilibrium, the vertical forces acting across any horizontal plane are balanced.

$$p = \gamma(1/R + 1/R') \quad (1)$$

$$2\pi r\gamma \sin \phi = V\sigma g + \pi x^2 p \quad (2)$$

where p = the pressure due to the curvature of the surface,

γ = the boundary tension,

R and R' = the two principal radii of curvature,

x = the horizontal distance to the axis of the drop,

ϕ = the angle between the normal and the axis,

V = the volume of fluid hanging from the plane,

σ = the difference in density between the two fluids, and

g = the acceleration of gravity.

² This equation originated with Thomas Young (56) and Pierre Laplace (26). A simple derivation is given by N. K. Adam (reference 1, pp. 8-9).

These equations may be combined and solved for γ in a number of ways. A satisfactory method is to pass a horizontal plane through the drop at the level where the profile curve passes through a point of inflection (figure 4).

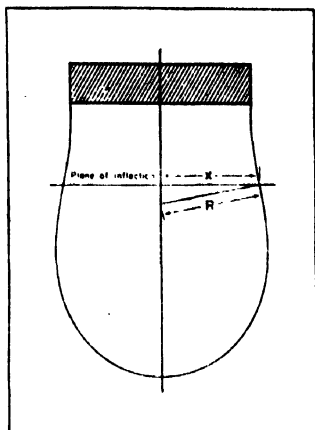


FIG. 4

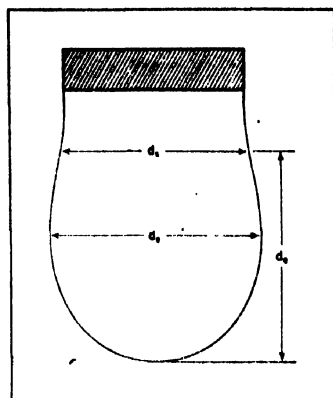


FIG. 5

FIG. 4. Method of the plane of inflection

FIG. 5. Method of the selected plane

The external radius of curvature, R' , is infinite at the plane of inflection, and therefore equation 1 reduces to

$$p = \frac{\gamma}{R}$$

Substituting this value of p in equation 2, and solving for the boundary tension, γ , we obtain for this special case,

$$\gamma = \frac{V\sigma g}{2\pi x \sin \phi - \frac{\pi x^2}{R}}$$

and since

$$\sin \phi = \frac{x}{R}$$

$$\gamma = \frac{g V \sigma R}{\pi x^2} \quad (3)$$

This equation is mathematically exact, but its use is subject to two severe limitations: (1) It is necessary to locate the true plane of inflection. This is a difficult graphical problem. If a plane is used which is slightly above the true plane of inflection, the measured value of V will be too large and the measured value of x will be too small. If a plane is used

which lies slightly below the true plane of inflection, the opposite will be true. In either case, a double error is introduced in the computed value of the boundary tension. (2) It is necessary to compute the volume of the drop from its profile. This is a tedious process which must either be done by graphical integration or with a special, very costly, planimeter. These practical difficulties limit the attainable precision of the "method of the plane of inflection" to about ± 2.0 per cent.

B. The method of a selected plane

A less direct method of attack leads to a more rapid and precise solution. It is first necessary to examine the differential equation of the surface of the drop.

If z is the vertical coördinate measured away from an origin placed at the point where the axis of rotation cuts the surface of the drop, and if b is the radius of curvature of the drop at the origin, the pressure due to the curvature is at any point equal to

$$p = \frac{2\gamma}{b} - g\sigma z \quad (4)$$

If equations 1 and 4 are combined, we obtain

$$\gamma(1/R' + 1/R) = \frac{2\gamma}{b} - g\sigma z$$

and the radii of curvature can be eliminated, since

$$R' = \frac{\left[1 + \left(\frac{dz}{dx}\right)^2\right]^{3/2}}{\frac{d^2z}{dx^2}}$$

and

$$R = \frac{x}{\sin \phi} = \frac{x \left[1 + \left(\frac{dz}{dx}\right)^2\right]^{1/2}}{\frac{dz}{dx}}$$

Then

$$\frac{\frac{d^2z}{dx^2}}{\left[1 + \left(\frac{dz}{dx}\right)^2\right]^{3/2}} + \frac{\frac{dz}{dx}}{x \left[1 + \left(\frac{dz}{dx}\right)^2\right]^{1/2}} = \frac{2}{b} - \frac{g\sigma z}{\gamma}$$

or

$$\frac{d^2 z}{dx^2} + \frac{dz}{x} \left[1 + \left(\frac{dz}{dx} \right)^2 \right] = \left[\frac{2}{b} - \frac{g\sigma z}{\gamma} \right] \left[1 + \left(\frac{dz}{dx} \right)^2 \right]^{3/2}$$

This is a second-order, second-degree differential equation whose integrated form is unknown. It can be reduced to the dimensionless form,

$$Z'' + \frac{Z'}{X} [1 + (Z')^2] = [2 - \beta Z] [1 + (Z')^2]^{3/2} \quad (5)$$

if we set

$$\beta = \frac{g\sigma b^2}{\gamma} \quad (6)$$

and let $X = x/b$, $Z = z/b$, $Z' = dZ/dX$, and $Z'' = d^2Z/dX^2$, which is equivalent to using b as the unit of length.

This derivation follows that of Bashforth and Adams (1, 3), with the exception that the algebraic signs of σ and of β are defined so as to be positive for pendant drops.

The differential equation 5 is seen to contain *two* parameters β and b , whose values identify the particular drop represented by the equation.

By rearranging equation 6, it is possible to express the boundary tension as a function of the two parameters β and b and of the effective specific weight ($g\sigma$). No method is known by which either β or b can be determined precisely and quickly from a picture of a drop. We must therefore transform equation 6 to a form which uses parameters whose values can be measured easily and accurately.

The size of a drop is most conveniently gauged by measuring its diameter at the equator, and the shape can be described by giving the ratio of the diameters measured at two different horizontal planes. If one diameter is at the plane of the equator, and the other is taken at a distance from the end of the drop equal to the equatorial diameter (figure 5), the shape can be described by the ratio,

$$S = \frac{d_e}{d_s} \quad (7)$$

where d_e is the diameter at the equator, and d_s is the diameter at the arbitrarily selected plane.

Figure 6 shows the useful range of drop shapes and will illustrate the way in which the shape ratio, S , varies from drop to drop. This figure was made from actual silhouette photographs of pendant drops. The black spots in the center are images of the light source caused by the liquid drop acting as an imperfect lens.

It has been shown that the quantities β and S are functions of the drop shape. A third quantity which is a function of the drop shape is the ratio of the diameter at the equator to the radius of curvature at the origin, d_e/b . Accordingly, we can define a new quantity,

$$H = \beta \left(\frac{d_e}{b} \right)^2 \quad (8)$$

which will be a function of S .

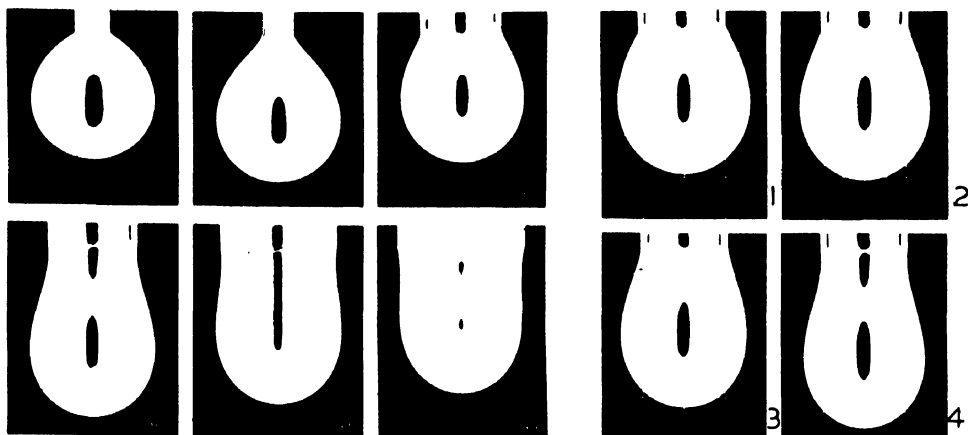


FIG. 6

FIG. 7

FIG. 6. Variation in the shape of pendant drops

FIG. 7. Change of shape of drop and surface tension with age. 0.025 per cent solution of sodium stearate in water at 25°C. (1) aged 10 sec., $S = 0.787$, $\gamma = 71.9$; (2) aged 60 sec., $S = 0.818$, $\gamma = 58.2$; (3) aged 120 sec., $S = 0.828$, $\gamma = 54.4$; (4) aged 1800 sec., $S = 0.849$, $\gamma = 39.2$.

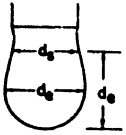
Equation 6 can now be solved for γ , combined with equation 8, and used in conjunction with a table of values of H as a function of S to determine the value of the boundary tension from a photograph of a pendant drop (table 1).

$$\gamma = \frac{g\sigma b^2}{\beta} = \frac{g\sigma(d_e)^2}{\beta \left(\frac{d_e}{b} \right)^2} = \frac{g\sigma(d_e)^2}{H} \quad (9)$$

Equation 9 is exact and convenient. Its precision depends upon the accuracy with which the linear measurements can be made and upon the labor which is expended in preparing the table of values of H as a function of S .

It is theoretically possible for this function to be evaluated mathematically, but the calculations are very laborious and unsatisfactory.

TABLE 1

Arithmetic tabulation of H-S function for pendant drops

$$S = \frac{d_r}{d_s}$$

S vs. $1/H$

$$\gamma = \frac{(\rho_1 - \rho_2) g d_s^2}{H}$$

Interpolation is unwarranted

S	0	1	2	3	4	5	6	7	8	9
0.70	0.797	0.795	0.792	0.790	0.787	0.785	0.782	0.780	0.777	0.775
0.71	0.772	0.770	0.767	0.765	0.762	0.759	0.757	0.754	0.752	0.749
0.72	0.747	0.744	0.742	0.739	0.737	0.735	0.732	0.730	0.727	0.725
0.73	0.722	0.720	0.718	0.715	0.713	0.711	0.709	0.706	0.704	0.702
0.74	0.699	0.697	0.695	0.692	0.690	0.688	0.685	0.683	0.681	0.679
0.75	0.676	0.674	0.672	0.670	0.668	0.665	0.663	0.661	0.659	0.657
0.76	0.655	0.652	0.650	0.648	0.646	0.644	0.642	0.640	0.637	0.635
0.77	0.633	0.631	0.629	0.627	0.625	0.623	0.621	0.619	0.617	0.615
0.78	0.613	0.611	0.609	0.607	0.605	0.603	0.601	0.599	0.597	0.595
0.79	0.593	0.591	0.589	0.587	0.585	0.583	0.581	0.579	0.577	0.575
0.80	0.573	0.571	0.570	0.568	0.566	0.564	0.562	0.561	0.559	0.557
0.81	0.555	0.553	0.551	0.550	0.548	0.546	0.544	0.542	0.540	0.539
0.82	0.537	0.535	0.533	0.532	0.530	0.528	0.526	0.524	0.523	0.521
0.83	0.519	0.518	0.516	0.515	0.513	0.511	0.509	0.507	0.506	0.504
0.84	0.502	0.501	0.499	0.498	0.496	0.494	0.493	0.491	0.490	0.488
0.85	0.486	0.485	0.483	0.482	0.480	0.479	0.477	0.476	0.474	0.473
0.86	0.471	0.470	0.468	0.467	0.465	0.464	0.462	0.461	0.459	0.458
0.87	0.457	0.455	0.454	0.452	0.451	0.450	0.448	0.447	0.446	0.444
0.88	0.443	0.441	0.440	0.439	0.437	0.436	0.434	0.433	0.431	0.430
0.89	0.429	0.428	0.426	0.425	0.423	0.422	0.420	0.419	0.418	0.417
0.90	0.415	0.414	0.413	0.411	0.410	0.409	0.408	0.406	0.405	0.404
0.91	0.403	0.401	0.400	0.399	0.398	0.396	0.395	0.394	0.393	0.391
0.92	0.390	0.389	0.388	0.386	0.385	0.384	0.383	0.382	0.381	0.379
0.93	0.378	0.377	0.376	0.375	0.373	0.372	0.371	0.370	0.369	0.368
0.94	0.366	0.365	0.364	0.363	0.362	0.361	0.359	0.358	0.357	0.356
0.95	0.355	0.354	0.353	0.352	0.351	0.350	0.349	0.348	0.346	0.345
0.96	0.344	0.343	0.342	0.341	0.340	0.339	0.338	0.337	0.335	0.334
0.97	0.333	0.332	0.331	0.330	0.329	0.328	0.327	0.326	0.325	0.324
0.98	0.323	0.322	0.321	0.320	0.319	0.318	0.317	0.316	0.315	0.314
0.99	0.313	0.312	0.311	0.310	0.309	0.308	0.307	0.306	0.305	0.304
1.00	0.303									

Methods of solution which have been attempted are based upon the use of finite increments or of series. They tend to be least satisfactory in the regions which are most important (3, 30, 31, 32, 33). However, an em-

pirical evaluation of the function is entirely feasible and adequate, and the function has been established to ± 0.2 per cent by measurements made on photographs of various sized drops of conductivity water having a known surface tension of 72.0 dynes per centimeter at 25°C. (table 1). The function has also been checked and found to be in agreement with the theoretical curves computed from the differential equation by Bashforth and Adams (3).

Experience shows that, if the linear dimensions of a drop can be measured with a probable error of not more than ± 0.1 per cent, this method will give values for the boundary tension which have an uncertainty of about ± 0.5 per cent. Measurement and calculation require about 10 min. per picture.³

EXPERIMENTAL APPLICATION

A number of boundary tension measurements were made on C.P. grade chemicals to obtain a comparison of the results obtainable by the method of pendant drops with results obtained by other methods and published in the literature. These results, given in abridged form in table 2, were calculated by the method of the selected plane, using table 1, which is based on the accepted value for the surface tension of water at 25°C. of 72.0 dynes per centimeter.

All of the pendant drop measurements reported in this table were made on surfaces 10 sec. old, while those given in the literature were made on surfaces whose age is not reported. It will be noted that the agreement between the two sets of surface tension data is good, since the surface tensions of pure, non-viscous liquids reach their ultimate equilibrium value very soon after the formation of a new surface. The agreement between the observed results and the published data on interfacial tension is less perfect, but these greater discrepancies are to be expected, since it is

³ Sample calculation of the surface tension of a pendant drop by the method of the selected plane:

Carbon tetrachloride in air at 25.0°C.; surface 15 sec. old.

Density of CCl_4	1.585 g. per cm. ³
Density of air.....	0.001 g. per cm. ³
Effective density.....	1.584 g. per cm. ³
Diameter of drop at equator, d_e	0.228 cm.
Diameter of drop at selected plane, d_s	0.224 cm.

$$S = \frac{d_s}{d_e} = 0.224/0.228 = 0.982$$

From table 1, $1/H = 0.321$

$$\gamma = \frac{g\sigma(d_s)^3}{H} = (0.321) (980.4) (1.584) (0.228)^3$$

$$= 26.0 \text{ dynes per centimeter}$$

The International Critical Tables, Vol. IV, p. 447, give for the surface tension of carbon tetrachloride at 25°C. the value 26.15 ± 0.1 dynes per centimeter.

generally recognized that the published values for interfacial tensions are frequently of low precision. Several causes are responsible for this. After a study of the sources of error which disturb standard methods and because of the relative freedom of the method of pendant drops from these difficulties, the new values are presented with the belief that they repre-

TABLE 2
Boundary tensions at 25°C.

BOUNDARY	TENSIONS IN DYNES PER CENTIMETER	
	Observed	In the literature
Benzene-air.....	28.1	28.4
Ethanol-air.....	21.9	21.9
Methanol-air.....	22.5	22.2
Toluene-air.....	27.7	27.8
Mercury-benzene.....	362.	355.
Mercury-water.....	369.	374.
Water-benzene.....	30.1	34.7
Water-carbon tetrachloride.....	43.8	44.5
Water-toluene.....	32.9	36.1

TABLE 3
Boundary tensions at 25°C.

BOUNDARY	TENSIONS IN DYNES PER CENTIMETER						AVERAGE VALUES
	17.6	17.3	17.6	17.4	17.5	17.3	
Ether-air.....	17.6	17.3	17.6	17.4	17.5	17.3	17.4
Ether-mercury.....	376.	389.	381.	380.	377.	375.	378.

TABLE 4
Boundary tensions at 25°C.

INTERFACE	TENSIONS IN DYNES PER CENTIMETER	
	Pendant down	Pendant up
Benzene-water.....	30.1	30.1
Carbon tetrachloride-water.....	43.8	43.9
Ether-water.....	11.2	10.9

sent the true interfacial tensions of the samples, as and when they were measured, within a probable error of not more than ± 1.0 per cent.

The results in table 2 are the averages of six determinations, each of which was made by measuring a *different* liquid drop. In table 3 the complete set of six measurements for diethyl ether-air and for diethyl ether-

mercury interfaces is given to show the consistency of a typical set of measurements.

It is not necessary for the fluid from which a drop is formed to wet the tip. For instance, drops of mercury can be suspended from a glass tip. The only difference is that in this case the drop will hang from the *inside* rather than from the *outside* of the glass tube. Drops may be supported by the tip in a number of ways. They may hang from the outer wall, from the outer rim, from the flat end, from the inner rim, or even from the inner wall of the tube. This does not in any way affect the applicability of the method or the precision of the results. It is necessary that the drop be supported in such a way that it is a solid of revolution, but the exact size, shape, or manner of support are determined by considerations of convenience alone.

Drops may be hung "pendant down," the heavier fluid inside the lighter, or "pendant up," the lighter fluid in the heavier. It will be seen from table 4 that the results are independent of whether the drops are hanging up or down.

SURFACE-ACTIVE SYSTEMS

If one or more of the components of a fluid system migrates into or out of an interface which is under observation, a change in the boundary tension with time can usually be detected. Likewise if some sort of surface structure is formed or if a chemical reaction is taking place at the interface, a similar change may be noted. If the boundary tension changes as the surface grows older, the surface is said to "age." Aging effects may cause the boundary tension of a fluid system to decrease to a small fraction of its initial value.

Data on the aging of aqueous solutions of sodium oleate and sodium stearate in contact with air and with mineral oil are illustrative of aging effects. The method of pendant drops is particularly suited to the determination of such data, since it makes it possible to obtain instantaneous determinations at any desired time intervals without disturbing the surface under observation.

Pendant drops of a solution containing a surface-active substance, such as sodium stearate, have a constant volume, but they exhibit a progressive change of shape with time due to the aging of their surfaces. This effect is shown in figure 7, which presents a series of photographs which were made in succession on a single drop.

Before presenting the results graphically, it will be well to examine typical data. In table 5, the results which were computed from two sets of pictures are given. Each set of values represents measurements made on a single drop, and the liquid hanging from the tip was completely replaced before the second drop was formed. In general, duplicate sets of measure-

ments were made for each solution which was studied, and the curves of figures 8 and 9 were plotted from the averages of these values.

It will be noted that there is good agreement between the two runs, even though the surface tension was changing quite rapidly and small errors in timing can produce considerable scattering in the results.

TABLE 5

Surface tension at 25°C. of a 0.025 per cent solution of sodium stearate in water
(See figures 7 and 10)

AGE IN SECONDS	SURFACE TENSION IN DYNES PER CENTIMETER	
	First drop	Second drop
5	70.8	72.2
10	71.9	71.6
15	69.7	66.3
30	62.9	63.4
60	58.2	56.9
120	54.4	54.6
240	51.6	50.7
480	47.3	45.8
960	42.8	42.6
1800	39.2	39.1
3600	36.0	35.7

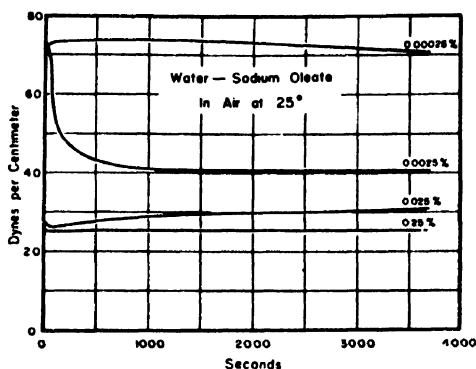


FIG. 8

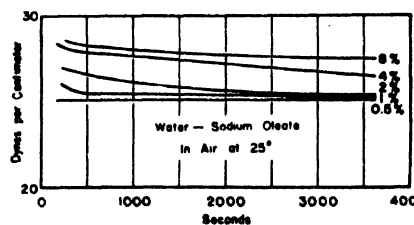


FIG. 9

FIG. 8. Change in surface tension of solutions of sodium oleate with time

FIG. 9. Change in surface tension of solutions of sodium oleate with time

Figure 8 shows the change, with time, of the surface tensions of solutions of sodium oleate. It will be noticed that extremely dilute solutions, 0.00025 or 0.0025 weight per cent, of this soap have an initial surface tension which is almost the same as that of pure water. During the first few seconds that the drop ages, the surface tension may increase. This is especially noticeable in the 0.00025 per cent curve, which rises rapidly,

levels off, and then slowly decreases. It remains at a value of slightly more than 72 dynes per centimeter for the first 3000 sec. The second sample in the series, containing 0.0025 per cent of sodium oleate, shows this same initial increase above the surface tension of pure water. However, in this case the rise is very rapid, and within the first 15 sec. the surface tension starts to fall rapidly, having approximately reached an asymptote after about 1500 sec. Still more concentrated solutions, 0.025 and 0.25 per cent, show a decrease during the first few seconds, which is followed by a slow recovery. The 0.025 per cent solution seems to be approaching the same asymptote as the 0.0025 per cent solution, but it is approaching it from the lower side.

A minimum surface tension is observed for a solution containing 0.5 per cent sodium oleate and the aging curve for this solution is a horizontal straight line⁴ (figure 9). More concentrated solutions have slightly higher surface tensions and all of them decrease with time, approaching the asymptote defined by the curve for the 0.5 per cent solution.

These results seem to indicate the existence of three different surface structures. One of these has a surface tension of about 74, the second has a surface tension of about 41, and the third has a surface tension of approximately 25 dynes per centimeter.

The explanation of these phenomena can undoubtedly be found in the concentration of soap in the interface resulting from surface activity. A freshly formed surface of a very dilute soap solution can be expected to have a surface tension very close to that of pure water, since the quantity of soap present in the new surface must be equal to the average throughout the drop. However, after a short interval of time has elapsed, enough soap will have collected in the interface to alter appreciably the boundary tension. As long as the concentration of soap in the interface remains sufficiently low, the molecules will exist in an ionized form, will behave as strong electrolytes, and will slightly raise the boundary tension. A further increase in the soap concentration will tend to change the soap molecules to an undissociated form and will cause a decrease in the boundary tension. Surface tensions greater than that of pure water may be explained by the presence of ionized soap.

The surface tension decreases rapidly as the concentration of soap in the interface increases, until a monomolecular or a colloidal film is formed. It is possible that the second type of surface is a structure of this kind.

Further concentration of soap in the interface increases the thickness of the film without greatly altering the surface tension. The minimum surface tension is probably reached when the film reaches an optimum colloidal thickness. A semi-solid "skin" is finally formed which gives

⁴ J. W. McBain *et al.* (38) have previously mentioned the existence of such a minimum.

rise to (a) an apparent increase in boundary tension, and (b) a surface structure so different from the condition of homogeneous, isotropic liquids assumed in the simple theory of surface tension that the meaning and interpretation of the results become a matter of some uncertainty. Before

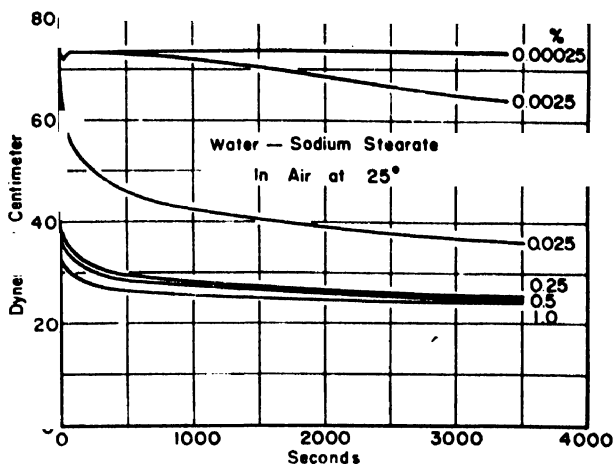


FIG. 10. Change in surface tension of solutions of sodium stearate with time

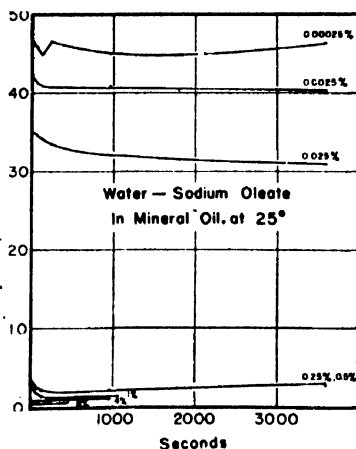


FIG. 11. Aging of the interface between aqueous solutions of sodium oleate and mineral oil

these hypotheses can be established definitely, it will be necessary to examine many other dilute solutions.

The curves for the aging of aqueous solutions of sodium stearate in air (figure 10) show a more uniform trend than do those for the oleate. As with sodium oleate, there appear to be at least two types of surface struc-

ture. More concentrated solutions could not be studied since they are semi-solid, anisotropic pastes.

Figure 11 shows the aging of the interface between several aqueous solutions of sodium oleate and mineral oil. The curves are qualitatively similar to those obtained for the aging of the same sodium oleate solutions in air, but it will be noted that the addition of a given amount of surface-active material causes a much greater percentage decrease in the interfacial tension than it does in the surface tension. For example, 1 per cent of sodium oleate reduces the equilibrium surface tension to 35 per cent, but it decreases the interfacial tension to 3 per cent of the no-soap value.

No concentration of sodium oleate was found which gives a minimum interfacial tension between the solution and the mineral oil. In this respect the interfacial tension results differ from the surface tension results, which show that a definite, minimum surface tension is obtained for solutions containing about 0.5 per cent of sodium oleate (38). This failure to find a minimum interfacial tension may be caused by the impossibility of examining sufficiently concentrated soap solutions.

The "break" in the 0.00025 per cent curve in figure 11 appears to be quite definite and to represent a real, sudden change in the surface of the drop. Similar effects have been observed in the aging of aqueous soap solutions in air. (Examine the 0.00025 per cent and 0.0025 per cent curves in figure 10.) The effect has only been observed with certain of the solutions, and, when it does occur, a second series of measurements always checks with the first. Unfortunately, the present data are too meager to throw much light on this curious effect. It is hoped that future work will reveal its cause.

SUMMARY

New work has demonstrated that the method of pendant drops provides a means for measuring either surface tension or interfacial tension which gives precise results under the most difficult conditions. The mathematical theory of the shape of static liquid drops is revised, and new methods are developed by which the boundary tension can be computed readily from a knowledge of the specific gravities of the liquids which are to be tested and from simple measurements made on a photograph which shows the silhouette of a hanging drop.

The construction of apparatus is discussed. With the equipment and empirical function now available, the method gives results which are comparable in speed and accuracy to the best obtainable by standard methods. With the present apparatus, the results have a probable error of about ± 0.5 per cent. The method is potentially capable of giving results accurate to ± 0.05 per cent. Future improvement depends upon a more precise determination of the mathematical function connecting drop shape

with boundary tension and upon the construction of special, high-precision equipment.

The method has the following outstanding advantages: (1) It is sufficiently simple to be subjected to a complete mathematical analysis. (2) The results are independent of the angle of contact between the fluid interface and the apparatus. (3) The method is static and is therefore not influenced by viscosity effects. (4) Measurements are made instantaneously. (5) Successive measurements can be made of a given surface without disturbing it, thus permitting an accurate study of the aging of surfaces. (6) Boundary tensions of any magnitude can be observed. Values as great as 370 dynes and as small as 0.3 dyne per centimeter were measured with the present apparatus. (7) Either surface tension or interfacial tension can be measured in any system in which at least one fluid is transparent and the fluids are of unequal density. (8) Only small samples are required. One cubic centimeter of the internal phase is usually more than enough for several measurements. (9) The apparatus is adapted to simple temperature control. (10) The photographs on which the measurements are made serve as permanent records.

Typical measurements are presented which show that: (1) The results are in agreement with those determined by standard methods and published in the literature. (2) The method gives self-consistent results for the boundary tensions of a great variety of liquid systems, of which some have not been reported previously. (3) The presence of surface-active materials can have a tremendous effect on the boundary tension, and liquid-liquid interfaces are relatively more affected by surface-active materials than are liquid gas interfaces. (4) Boundary tensions may either increase or decrease during the aging of an interface.

Preliminary suggestions as to the possible reasons for the observed phenomena are offered.

The results so far obtained justify the belief that the method of pendant drops will prove to be of special value in studying the boundary tensions of (1) viscous liquids, (2) surface-active solutions, (3) small samples of rare chemicals, and (4) systems in which the contact angle is not zero.

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CONVENTIONS AND ASSUMPTIONS IN THE INTERPRETATION OF EXPERIMENTAL DATA BY MEANS OF THE GIBBS ADSORPTION THEOREM¹

PIERRE VAN RYSSELBERGHE

Department of Chemistry, Stanford University, California

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I. INTRODUCTION

Various conventions used in the interpretation of surface tension data by means of the Gibbs adsorption theorem (4) have been discussed in a number of recent contributions, such as those of Guggenheim and Adam (5), Butler and Wightman (2), and Rice (8). We shall briefly recall the essential points of these methods. Let us consider a two-component, two-phase system, for instance, a binary solution and its mixed vapor, separated from each other by a plane interface. The Gibbs adsorption theorem (4) states that, when the inhomogeneous layer at the interface is in complete equilibrium with the liquid and the vapor phase at a given temperature,

$$d\sigma = -\Gamma_1 d\mu_1 - \Gamma_2 d\mu_2 \quad (1)$$

in which σ is the surface tension of the solution, μ_1 and μ_2 the molar chemical potentials of the two components, and Γ_1 and Γ_2 the surface excesses in moles per unit area. It has been demonstrated by Gibbs (4) that, when the mathematical dividing surface is plane, equation 1 is invariant in form with respect to a change in the position of this surface and $d\sigma$ has the same value for all positions of the surface. The surface excesses Γ_1 and Γ_2 , on the contrary, depend on the position of the surface, but the expression $\Gamma_1 \frac{N_2}{N_1} - \Gamma_2$, in which N_1 and N_2 are the mole fractions of the bulk solution, is invariant with respect to a change in the position of the dividing surface, since, on account of the Gibbs-Duhem formula

$$N_1 d\mu_1 + N_2 d\mu_2 = 0 \quad (2)$$

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(in which the concentrations of both components in the vapor phase are neglected), formula 1 may be rewritten

$$d\sigma = \left(\Gamma_1 \frac{N_2}{N_1} - \Gamma_2 \right) d\mu_2 \quad (3)$$

The two differentials $d\sigma$ and $d\mu_2$ being invariant, the expression

$$\Gamma_1 \frac{N_2}{N_1} - \Gamma_2$$

is also invariant. A special position of the mathematical dividing surface corresponds to what Gibbs has called the "surface of tension," for which certain equations have "the same form as if a membrane without rigidity and having a tension σ , uniform in all directions, existed at the dividing surface" (4, page 229). Defay (3) has established the conditions of mechanical equivalence between the real system with an inhomogeneous layer of finite thickness and the idealized system in which the two phases are separated by the surface of tension. These conditions are only of theoretical interest and cannot yield explicit information concerning the exact position of the surface of tension until the complete structure of the layer and the distribution of tensions are known. Let us note, however, that even in the case of plane interfaces, in spite of the invariance of σ , there is a definite surface of tension, determined, as shown by Defay (3), by conditions of equivalence of total torques. It is necessary, however, to have recourse to other dividing surfaces if one wishes to calculate values of Γ_1 and Γ_2 from which some information as to the structure of the layer can be derived.

It is customary to locate the dividing surface in such a manner that the surface excess Γ_1 of the solvent is equal to zero and to calculate the surface excess Γ_2 of the solute from the formula

$$\Gamma_2^{(1)} = - \frac{d\sigma}{d\mu_2} \quad (4)$$

which gives us a convenient and suggestive method of recording the results of surface tension measurements. If, however, one wishes more precise information concerning the inhomogeneous layer, it is preferable to put the dividing surface immediately underneath the layer. Since the concentrations in the vapor phase are neglected, the values of Γ_1 and Γ_2 represent the total amounts of components 1 and 2 present in a column of 1 cm.² cross section on top of the homogeneous liquid. So far, we have only one equation to determine the unknowns Γ_1 and Γ_2 , namely, the Gibbs theorem 3. We thus have to set up a second relationship between Γ_1 and Γ_2 .

For instance, we may assume that the layer is one molecule thick and write

$$\Gamma_1 A_1 + \Gamma_2 A_2 = 1 \quad (5)$$

in which A_1 and A_2 are the areas per mole of each component. Guggenheim and Adam (5) and also Butler and Wightman (2) have shown, in the case of water-alcohol mixtures, that the simultaneous equations 3 and 5 yield reasonable values of Γ_1 and Γ_2 when plausible constant values of A_1 and A_2 are adopted and all other disturbing effects are neglected. The surface mole fraction $\Gamma_2/\Gamma_1 + \Gamma_2$ obtained by these authors is not steady and exhibits a slight maximum before increasing to the value 1 in pure alcohol. Guggenheim and Adam (5) ascribe this effect to a possible lack of constancy of the molar areas A_1 and A_2 , while Butler and Wightman (2) suggest that the layer may not be truly monomolecular.

Various mixture rules for the surface tension of binary solutions have been used in the older work on the subject without any reference to the Gibbs adsorption theorem. For instance, Morgan and Griggs (6) and Morgan and Scarlett (7) use the mixture rule

$$\sigma = x\sigma_1 + (1 - x)\sigma_2 \quad (6)$$

in which σ_1 and σ_2 are the surface tensions of the pure liquids, and x and $1 - x$ the percentages by weight of the components in the bulk solution. No discussion of adsorption at the interface is presented, and the Gibbs theorem is not mentioned. Whatmough (9) used mixture rules of the same type, but took for x and $1 - x$ mole fractions, weight fractions, or volume fractions of the bulk solution, again without reference to the phenomenon of adsorption.

In this paper we wish to present and discuss the simplest possible mixture rule in which adsorption is taken into account, namely

$$\sigma = \frac{\Gamma_1 \sigma_1 + \Gamma_2 \sigma_2}{\Gamma_1 + \Gamma_2} \quad (7)$$

This formula is derived from the logical assumption that the Γ_1 and Γ_2 values actually responsible for the surface tension will contribute, as a first approximation, the portions

$$\frac{\Gamma_1}{\Gamma_1 + \Gamma_2} \sigma_1 \quad \text{and} \quad \frac{\Gamma_2}{\Gamma_1 + \Gamma_2} \sigma_2$$

to the total surface tension σ . The Gibbs theorem 3 and our formula 7 are simultaneous equations, the unknowns being Γ_1 and Γ_2 .

II. DISCUSSION OF THE MIXTURE RULE AND OF THE GIBBS ADSORPTION THEOREM

The terms "positive adsorption" and "negative adsorption" of the solute at the surface of the solution are based upon the sign of $\Gamma_2^{(1)}$ of formula 4, which is obviously opposite to that of $d\sigma/d\mu_2$ or also opposite to that of $d\sigma/dN_2$, since $d\mu_2/dN_2$ is always positive. From formula 3, however, nothing can be said about the sign of Γ_2 until Γ_1 is known, or *vice versa*. Our mixture rule (equation 7) requires both Γ_1 and Γ_2 to be positive. We shall associate the terms "positive adsorption" and "negative adsorption," respectively, with the following two inequalities

$$\frac{\Gamma_2}{\Gamma_1 + \Gamma_2} > N_2 \quad \frac{\Gamma_2}{\Gamma_1 + \Gamma_2} < N_2 \quad (8)$$

Formula 7 gives

$$\frac{\Gamma_2}{\Gamma_1} = \frac{\sigma_1 - \sigma}{\sigma - \sigma_2} \quad \text{and} \quad \frac{\Gamma_2}{\Gamma_1 + \Gamma_2} = \frac{\sigma_1 - \sigma}{\sigma_1 - \sigma_2} \quad (9)$$

Combining equations 3 and 7 we get

$$\frac{d\sigma}{d\mu_2} = \Gamma_2 \left[\frac{\sigma - \sigma_2}{\sigma_1 - \sigma} \cdot \frac{N_2}{N_1} - 1 \right] \quad (10)$$

Now, Γ_2 being positive, we have

$$\frac{\sigma - \sigma_2}{\sigma_1 - \sigma} \cdot \frac{N_2}{N_1} - 1 \geq 0 \quad \text{when} \quad \frac{d\sigma}{d\mu_2} \geq 0 \quad (11)$$

or also

$$\frac{\Gamma_2}{\Gamma_1 + \Gamma_2} = \frac{\sigma_1 - \sigma}{\sigma_1 - \sigma_2} \geq N_2 \quad \text{when} \quad \frac{d\sigma}{d\mu_2} \leq 0 \quad (12)$$

Our mixture rule is, therefore, in agreement with the familiar interpretation of the Gibbs theorem based upon the convention $\Gamma_1 = 0$.

Figure 1 corresponds to positive adsorption of alcohol (component 2) at the surface of water-alcohol mixtures. The curve represents the surface tension plotted against the bulk mole fraction N_2 ; the straight line represents the surface tension plotted against the surface mole fraction $\Gamma_2/\Gamma_1 + \Gamma_2$. The analogy with phase rule diagrams is obvious. If the surface tension curve exhibits a minimum or a maximum at some particular composition (N_1^0 , N_2^0) our mixture rule cannot be applied without modification. At the extremum we have

$$\frac{d\sigma}{d\mu_2} = \frac{d\sigma}{dN_2} \cdot \frac{dN_2}{d\mu_2} = 0 \quad (13)$$

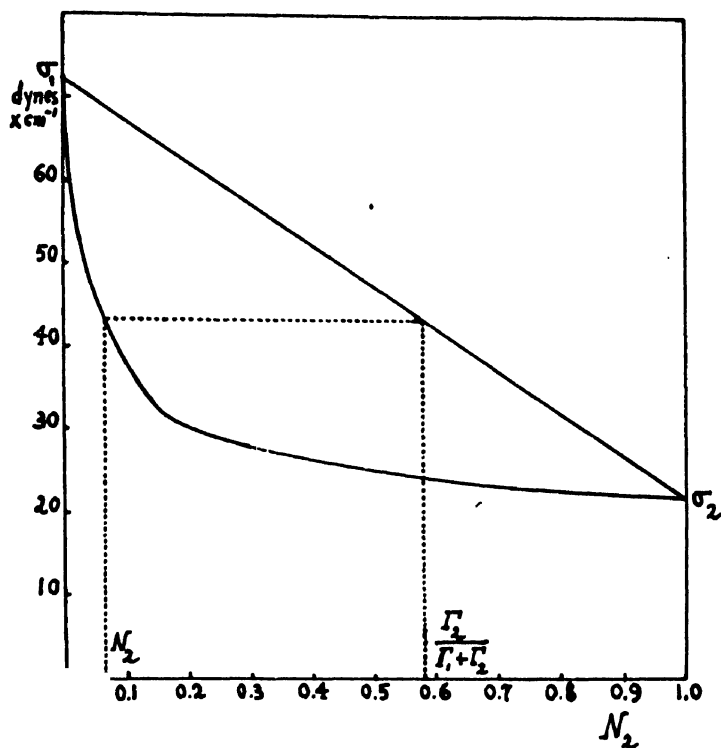


FIG. 1. Surface tension of water-alcohol mixtures plotted against bulk and surface mole fraction of alcohol

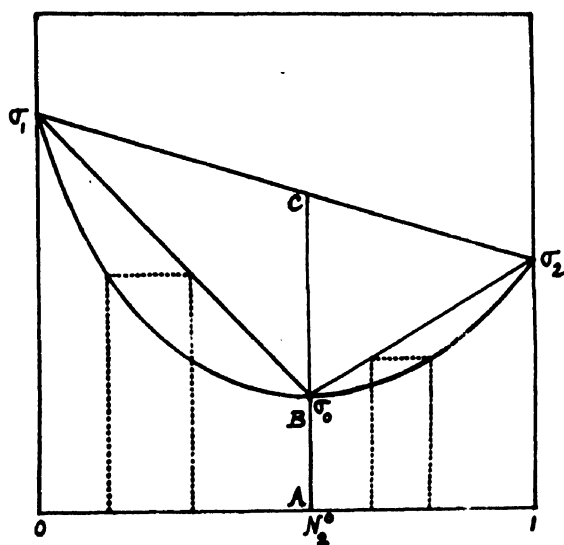


FIG. 2. Surface tension curve exhibiting a minimum

and, according to equation 3,

$$\frac{\Gamma_2^0}{\Gamma_1^0} = \frac{N_2^0}{N_1^0} \quad \text{or} \quad \frac{\Gamma_2^0}{\Gamma_1^0 + \Gamma_2^0} = N_2^0 \quad (14)$$

In other words, the surface mole fraction and the bulk mole fraction are identical at the extremum. We should have, according to our mixture rule,

$$\sigma_0 = N_1^0 \sigma_1 + N_2^0 \sigma_2 \quad (14)$$

which is impossible, since it would require the segments AB and AC of figure 2 to be equal. We can, however, overcome this difficulty by applying the mixture rule separately between σ_1 and σ_0 and between σ_0 and σ_2 . We then have positive adsorption of the mixture N_2^0 between σ_1 and σ_0 and negative adsorption of this mixture between σ_0 and σ_2 . The analogy with the boiling point diagram of an azeotropic mixture is obvious.

III. INTERPRETATION OF SURFACE TENSION DATA FOR WATER-ALCOHOL MIXTURES AND DESCRIPTION OF THE SURFACE LAYER

In order to test the plausibility and usefulness of our mixture rule we now present a new interpretation of the surface tension data of water-alcohol mixtures. The values of $d\sigma/d\mu_2$ are obtained from the paper of Guggenheim and Adam (5), where $-d\sigma/d\mu_2$ is called $\Gamma_2^{(1)}$, being the value of Γ_2 corresponding to the usual convention $\Gamma_1 = 0$. The values of σ are those of Bircumshaw (1). Similar values for both σ and $d\sigma/d\mu_2$ were obtained by Butler and Wightman (3). In table 1 we give, for a series of mole fractions N_2 of alcohol, the surface tension σ in dynes per centimeter, the derivative $d\sigma/d\mu_2$ in moles per cm^2 , the surface excesses Γ_1 and Γ_2 as calculated by means of our formulas 7 and 10, in moles per cm^2 , the surface mole fraction $\Gamma_2/\Gamma_1 + \Gamma_2$, and the area A_2 in cm^2 occupied by one mole of alcohol and calculated as indicated below. The temperature is 25°C .

Our values of Γ_1 and Γ_2 are of the right order of magnitude for a monomolecular layer. A comparison with those obtained by Guggenheim and Adam (5) from equation 5 shows that, while their values of Γ_2 increase with N_2 , our values decrease, indicating that the area occupied per mole of alcohol increases with N_2 . This area is constant in Guggenheim and Adam's calculations. Their values of Γ_1 decrease when N_2 increases and so do ours, but our Γ_1 's are smaller, in agreement with the idea of an increasing area for the alcohol molecules, since the area of water molecules can probably be assumed constant and independent of possible changes of orientation, while the area occupied by alcohol molecules will vary considerably, the two extreme cases being molecules standing up on the

surface and molecules lying flat on it. We have calculated the area occupied by one mole of alcohol at the various mole fractions N_2 by assuming the area A_1 for water to be 0.06×10^{10} cm.² per mole, i.e., the second of the three values considered by Guggenheim and Adam (5). The results are reported in the last column of table 1. Extrapolating to $N_2 = 0$ we see that the limiting value of A_2 is in perfect agreement with the value 0.12×10^{10} cm.² per mole adopted by Guggenheim and Adam (5) for molecules of alcohol oriented perpendicularly to the surface. Extrapolating to $N_2 = 1$ we find $A_2 = 0.45 \times 10^{10}$ cm.² per mole, a result which would indicate that in pure alcohol most of the molecules are lying flat on the surface. The intermediate values of A_2 can be considered as giving a measure of the average orientation of alcohol molecules at the surface. It is of course true that, if orientation changes with concentration, the

TABLE 1
Surface tension and surface composition of water-alcohol mixtures

N_2	σ	$-\frac{d\sigma}{d\mu_2} \times 10^{10}$	$\Gamma_1 \times 10^{10}$	$\Gamma_2 \times 10^{10}$	$\frac{\Gamma_2}{\Gamma_1 + \Gamma_2}$	$A_2 \times 10^{-10}$
0	72.2	0.0	(16.7)	0	0	(0.12)
0.05	45.0	5.85	5.2	6.1	0.54	0.11
0.1	36.4	6.3	2.65	6.6	0.715	0.13
0.2	29.7	6.45	1.2	6.75	0.845	0.135
0.3	27.6	5.9	0.78	6.25	0.89	0.155
0.4	26.35	5.1	0.52	5.45	0.915	0.18
0.5	25.4	4.25	0.33	4.6	0.935	0.215
0.6	24.6	3.4	0.20	3.7	0.95	0.265
0.7	23.85	2.9	0.12	3.2	0.965	0.31
0.8	23.2	2.5	0.07	2.75	0.975	0.36
0.9	22.6	2.2	0.03	2.45	0.99	0.405
1.0	22.0	2.1	0.00	(2.2)	1.00	(0.45)

values of σ_2 in the mixture rule (7) also depend on concentration, but in an unknown manner. It is, however, probable that such a variation is small and that our interpretation of surface tension data is just as plausible as that based upon the initial assumption of a monomolecular layer and upon the corresponding formula (formula 5) in which the area A_2 is considered as constant. The mole fractions $\Gamma_2/\Gamma_1 + \Gamma_2$ reported in table 1 increase with N_2 in a continuous and steady manner, as is shown on figure 3 by the heavy curve I, while the dotted curve II represents the mole fractions obtained by Guggenheim and Adam (6) for $A_1 = 0.06 \times 10^{10}$. Similar results were obtained by these authors with $A_1 = 0.04 \times 10^{10}$ and 0.08×10^{10} , A_2 being 0.12×10^{10} in the three cases. It is interesting to note that our interpretation of the composition of the surface layer agrees with a suggestion made by Rice (8, page 573): "Now it might happen

that with increasing concentration of alcohol, the more polar water molecules being replaced by weaker alcohol molecules, there would be a decrease in orientation with an increase in area occupied, caused by each alcohol molecule lying flat in the surface."

It is interesting to note that the distance between our dividing surface and that corresponding to $\Gamma_1 = 0$ varies from 1.09 Å. for $N_2 = 0.05$ to 0.16 Å. for $N_2 = 0.9$. A displacement of the dividing surface smaller than the thickness of a monomolecular layer has thus a profound influence on

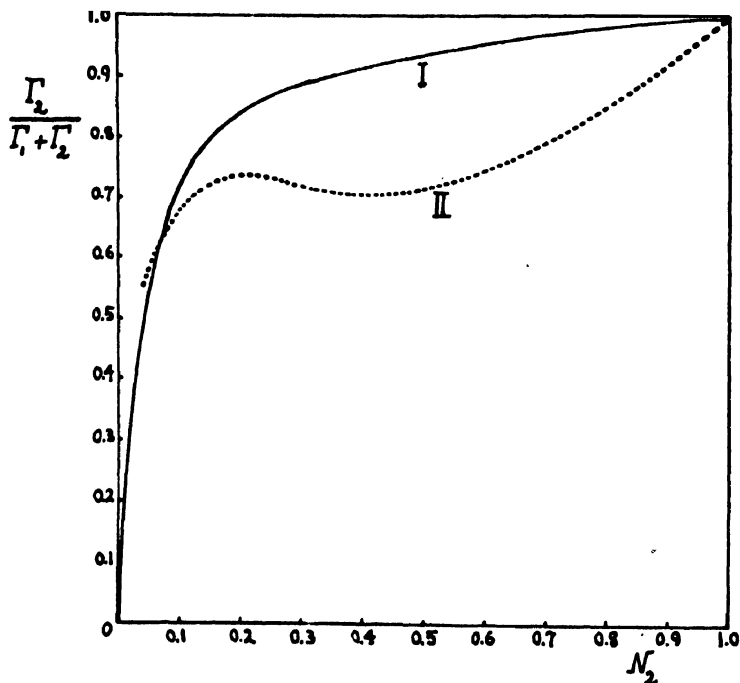


FIG. 3. Surface mole fraction of alcohol plotted against bulk mole fraction in water-alcohol mixtures

the values of Γ_1 and Γ_2 . When the surface corresponding to $\Gamma_1 = 0$ is used we are unable to obtain any information regarding the amount of component 1 which, together with the amount Γ_2 of component 2, is responsible for the surface tension, while our mixture rule gives a first approximation for both Γ_1 and Γ_2 .

IV. SUMMARY

1. Conventions and assumptions in the interpretation of surface tension data of binary mixtures are briefly discussed. The concept of surface of tension is recalled.

2. A mixture rule for the surface tension of binary mixtures involving

the surface excesses of both components is proposed. This rule and the Gibbs adsorption theorem form a system of two simultaneous equations in which these surface excesses are the unknowns.

3. It is shown that the mixture rule agrees with the familiar concepts of positive and negative adsorption usually defined by means of the convention $\Gamma_1 = 0$. The case of surface tension curves with an extremum is discussed separately.

4. The method is applied to water alcohol mixtures. The results show that the surface mole fraction of alcohol increases rapidly and steadily when the bulk mole fraction increases, that the surface excess of water decreases rapidly, that the surface excess of alcohol decreases after passing through a maximum near $N_2 = 0.2$. If the inhomogeneous layer is monomolecular, the alcohol molecules, oriented perpendicularly to the surface in very dilute solutions, lie flat on the surface in pure alcohol.

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STUDIES IN COLLOIDAL CLAYS. I¹

E. A. HAUSER AND D. S. LE BEAU²

*Department of Chemical Engineering, Massachusetts Institute of Technology,
Cambridge, Massachusetts*

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Only in recent years has it been possible to produce for the purpose of further studies well-defined monodisperse fractions of colloidal clays by rational supercentrifugal separation (2, 3).

The lack of data concerning, primarily, clay sols of low concentration and varying particle sizes made highly desirable a closer study of *freshly* prepared natural suspensions of the clay mineral montmorillonite (the major constituent of bentonite) in concentrations from about 0.06 to 2 per cent by weight.

Of special interest was the question whether any signs of structure could be detected in such low concentrations and, if so, how these change with particle size of the suspension and also what effect certain pretreatments of the original suspensions, as, for instance, thermal concentration at different temperatures, would have on their properties. Changes due to the addition of electrolyte have not been considered in this investigation, but will be discussed separately in a later publication.

The particular bentonite used in this work was of the Wyoming type, mined by the American Colloid Co., Chicago, Illinois. (For further details as to location of the deposit, see reference 3.)

The analysis of the finest fraction of this bentonite gave the values in table 1.

The different particle size fractions were produced according to a method described by Hauser and Reed (2). Six fractions were obtained. The gels produced by supercentrifuging had about 10 per cent dry weight content. They were stored in the condition in which they were scraped from the liner of the centrifuge. The overflow of the finest and final fraction was collected and stored as a sol of 0.46 per cent dry weight. It will be referred to as fraction 7.

The following experiments were carried out with fraction 6 containing particles of an average apparent diameter of 14 m μ . Comparative studies

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² Present address: Dewey & Almy Chemical Co., Cambridge, Massachusetts.

were also made with fraction 4 (average apparent particle diameter = 28 $m\mu$) and fraction 2 (average apparent particle diameter = 48 $m\mu$) and fraction 7. (This sol contains only particles of an apparent diameter below 14 $m\mu$.)

PREPARATION OF STANDARD SOLS

Sols varying in concentration from 0.06 to 2 per cent dry weight of bentonite were made up from fractions 6, 4, and 2, by careful dilution of the gels obtained by supercentrifuging with conductivity water, to approximately the desired concentrations. The exact concentrations of these dispersions of known apparent particle size were determined gravimetrically by evaporation to constant weight at 105°C.

TABLE 1
Composition of the bentonite

	<i>per cent</i>
Loss at 105°C.	6.20
SiO ₂	58.88
Fe ₂ O ₃	2.86
Al ₂ O ₃ , Mn ₂ O ₄ , P ₂ O ₅	26.16
CaO	0.80
MgO	2.67
Na ₂ O/K ₂ O as Na ₂ O	2.13
SO ₃	Not determined
	99.78

Finally, a dispersion of fraction 6 of only 0.077 per cent dry weight was produced for the purpose of studying the influence of temperature on property changes of sols obtained by concentration instead of dilution. This standard dispersion was reconcentrated by means of thermal evaporation at 75°C. and 95°C. to approximately the same concentrations as obtained by dilution of the original gels.

APPARENT SPECIFIC GRAVITY AT 25°C.

All determinations were carried out with a simple type of pycnometer, this having been found most suitable for the work. All precautions essential in obtaining accurate results as, for example, temperature control provided by a thermostat sensitive to $\pm 0.01^\circ\text{C}$., perfect cleanliness, freedom from air bubbles in the sols, etc., were carefully observed.

The apparent specific gravity was determined as follows:

$$W_s - W_B = W_w \quad (1)$$

$$V_p - V_w = V_B \quad (2)$$

$$\frac{W_B}{V_B} = \text{apparent specific gravity}$$

where W_s = weight of suspension in pycnometer (25°C.),

W_B = weight of bentonite present in W_s , as known by dry weight determinations,

V_p = volume of pycnometer (at 25°C.),

V_w = volume of water in suspension (25°C.), and

V_B = apparent volume of bentonite in suspension

The apparent specific gravities of seven dispersions of fraction 6, all obtained by dilution varying in per cent dry weight from 0.067 to 1.939 are given in table 2.

It can be seen that, starting with the most dilute dispersion which gives a value slightly below the one generally recorded in literature for dry bentonite (2.6-2.7), there is a continuous increase in apparent specific gravity. It is more pronounced in the lower concentrations than in the

TABLE 2
Apparent specific gravities (25°C.) of seven dispersions of fraction 6

CONCENTRATION IN PER CENT DRY WEIGHT	APPARENT SPECIFIC GRAVITY
0.067	2.580
0.152	2.714
0.368	2.773
0.710	2.796
1.146	2.845
1.506	2.860
1.643	2.861
1.939	2.861

higher ones. From concentrations above 1.5 per cent dry weight the apparent specific gravity approaches an asymptotic value. Since the specific gravity of a substance is determined by the term $\frac{\text{weight}}{\text{volume}}$, it should be a constant, independent of the amount (weight) of the substance used. The actual weight of the bentonite present in any of the dispersions studied being known, the only variable left is its apparent volume, since the determination of the volume of bentonite present in the suspension is an indirect one. The calculated values for the apparent volume turn out to be smaller than the volume as computed when using the dry specific gravity of bentonite. This can be explained by assuming that the amount of water present in the pycnometer when filled with the *suspension* is in excess of the theoretical amount needed to fill the pycnometer containing a known volume of bentonite. Therefore, the surplus of the water must be strongly adsorbed and compressed on to the surface of the bentonite particles.

As a further consequence of this deduction one would have to expect that the apparent specific gravity will decrease inversely with the particle size of the sols studied. Increasing particle size results in a decrease of available surface area of the disperse phase. The apparent specific gravities³ for fractions 4 and 2, respectively, are recorded in tables 3 and 4 (figure 1).

As can be seen, fraction 4—although here, too, an increase in apparent specific gravity with increasing concentration is noticeable—does not

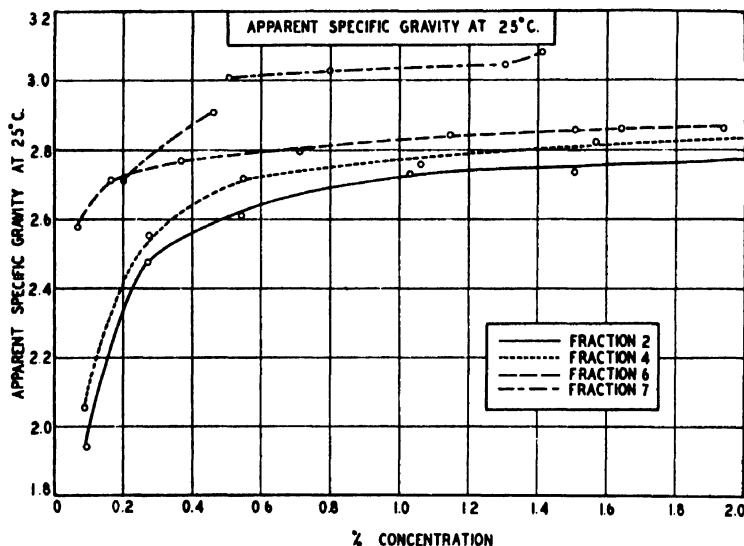


Fig. 1. Apparent specific gravities for fractions 2, 4, 6, and 7 at 25°C.

reach the values of fraction 6. Fraction 2 in turn gives lower apparent specific gravities than fraction 4. However, up to a concentration of 2 per cent, none of these fractions approaches a constant value, as fraction 6 did. This can be explained by the presence, at a given concentration, of a smaller surface area available for adsorption in fraction 2 than in 4, and in fraction 4 than in fraction 6.

³ For the determination of the apparent specific gravity, two pycnometers were always used. Each pycnometer was filled and weighed four different times. Each series consisted of four weighings, and the weights checked within 0.0002 g. The apparent specific gravities calculated from the average of each series were checked with a series using the second pycnometer. Even in the most dilute dispersions the differences in weight between the pycnometer filled with the suspension and the pycnometer filled with distilled water were never less than 0.0020 g. With this method the calculated maximum error in the most dilute suspension studied is ± 5 per cent. Therefore, given a value of 1.94 for the apparent specific gravity of the most dilute dispersion of fraction 2, the possible deviation can be between 1.84 and 2.04. With increasing concentration of the suspension the maximum possible error naturally decreases rapidly.

The figures shown in tables 3 and 4 demonstrate that the most dilute suspensions exhibit a value for the apparent specific gravity which is lower than the one generally accepted for dry bentonite. Similar results were found by van Bemmelen (5) when determining the apparent specific gravity of silica gel containing different amounts of water. Minima in apparent specific gravity could be found with silica gels having a maximum amount of water content, as well as with those containing a minimum amount of water, whereas in medium concentrations the apparent specific gravity rose.

Since only the range of very dilute suspensions has been studied in this investigation, no second minimum in apparent specific gravity can be expected. However, the asymptotic value obtained in higher concentrations of fraction 6 might point to this effect in case the concentration were further increased.

TABLE 3

*Apparent specific gravities of fraction
4 at 25°C.*

CONCENTRATION IN PER CENT DRY WEIGHT	APPARENT SPECIFIC GRAVITIES
0.086	2.054
0.273	2.544
0.548	2.718
1.063	2.762
1.573	2.827
2.033	2.842

TABLE 4

*Apparent specific gravities of fraction
2 at 25°C.*

CONCENTRATION IN PER CENT DRY WEIGHT	APPARENT SPECIFIC GRAVITIES
0.094	1.941
0.270	2.477
0.544	2.609
1.035	2.731
1.505	2.732
2.040	2.782

When the dilute suspension of fraction 6 was reconcentrated by evaporation at 75°C. (table 5) and the apparent specific gravities were determined, the increase in apparent specific gravity, especially in low concentrations, never reached the value of the untreated sample, although it was still observable. During thermal evaporation partial agglomeration of primary particles takes place. This has been confirmed by ultramicroscopic studies. Such agglomeration increases the effective particle size of the suspension as well as the apparent volume of the disperse phase, while the available active surface decreases. The stability of a sol which has been obtained by dilution from a stable gel will increase with increasing concentration of the disperse phase. Less agglomerates will form, i.e., more active surface will be available; moreover the available surface automatically increases with concentration. Therefore, the apparent specific gravity must increase.

Reconcentration of the dilute suspension of fraction 6 at 95°C. (table 6)

shows a similar decrease in apparent specific gravity in lower concentrations (figure 2).

Fraction 7 is a sol containing, as previously mentioned, particles of an average particle size diameter below 14 μ . Since its dry weight content was only 0.46 per cent, it was necessary to concentrate it by evaporation.

TABLE 5

Apparent specific gravities at 25°C. of fraction 6, reconcentrated at 75°C.

CONCENTRATION IN PER CENT DRY WEIGHT	APPARENT SPECIFIC GRAVITIES
0.153	2.460
0.306	2.682
0.512	
0.046	2.716
1.358	2.728

TABLE 6

Apparent specific gravities at 25°C. of fraction 6, reconcentrated at 95°C.

CONCENTRATION IN PER CENT DRY WEIGHT	APPARENT SPECIFIC GRAVITIES
0.283	2.617
0.583	2.695
1.118	2.744

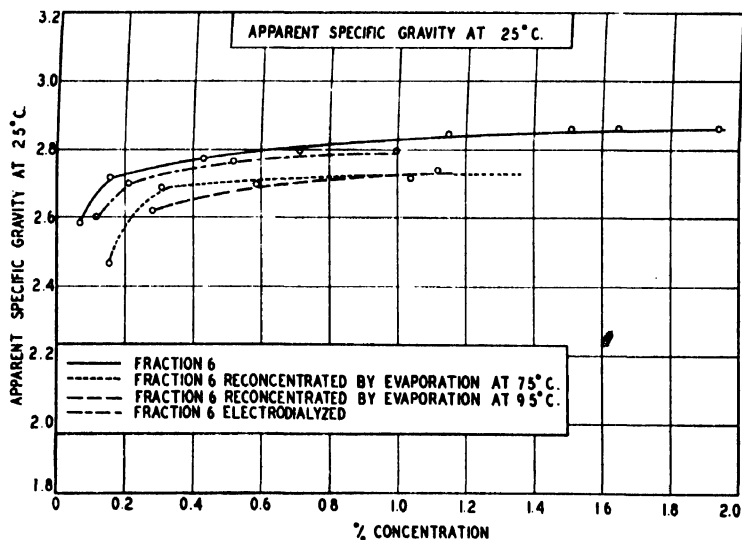


FIG. 2. Apparent specific gravities of fraction 6 at 25°C.

Only one dispersion was produced by dilution for the specific purpose of studying a concentration lower than 0.46 per cent. The results are given in table 7.

Here, too, an increase in apparent specific gravity with concentration can be found. As was to be expected with a system containing extremely fine particles, the original dispersion already has a higher apparent specific gravity than any of the fractions so far discussed. The sol obtained by dilution exhibits an apparent specific gravity corresponding to the one

accepted for the dry material. This system is very dilute and the particles most probably are monoplates, so that neither appreciable interlamellar swelling nor adsorption can take place. However, the first of the series of reconcentrated dispersions (0.505 per cent) reveals a sudden and remarkable increase in apparent specific gravity. The apparent specific gravities are extremely high and are still rising at a concentration of 1.41 per cent. These sols also reveal a pronounced increase in viscosity and exhibit high yield values. These data substantiate the fact already established by Hauser and Reed (3) that the tendency to form gels increases with decreasing particle size. The formation of a strong thixotropic gel without the addition of electrolyte at a concentration of only 1.41 per cent dry weight is, to our knowledge, the lowest figure so far recorded. The above data, if viewed in the light of the previous discussion, indicate further that increased adsorption of the dispersing medium on the dispersed particles,

TABLE 7
Apparent specific gravities at 25°C. of fraction 7

CONCENTRATION IN PER CENT DRY WEIGHT	APPARENT SPECIFIC GRAVITIES
0.201*	2.710
0.460†	2.911
0.505‡	3.007
0.798‡	3.028
1.303‡	3.042
1.410‡	3.081

* Sol obtained by dilution of the original sol.

† Original sol.

‡ Original sol concentrated at 95°C.

as indicated by the abnormal increase in apparent specific gravities (formation of large water hulls), is a predominant factor in the gelation of colloidal clay suspensions of low concentration.

DETERMINATIONS OF ABSOLUTE VISCOSITIES

A Hoesppler viscosimeter (4) was used, which permits a quick determination of absolute viscosities over a fairly large range. The method is based on the principle of a ball rolling down the wall of a glass tube inclined 10° from the vertical. The ball travels in a guided and predetermined eccentric position through the tube, so that uncontrollable wall effects and the influence of turbulent flow are avoided. The determinations of viscosity were carried out at 25°C. and 40°C.

In the very dilute sols up to 0.27 per cent dry weight only small differences in the viscosities of fractions 2 and 4 can be found. Fraction 6 (table 10) is slightly higher in viscosity than fractions 4 (table 9) and 2

(table 8), and fraction 7 again is slightly higher than fraction 6 (figure 3), With such low concentrations no great differences were to be expected. owing to the small number of particles present. With increasing con-

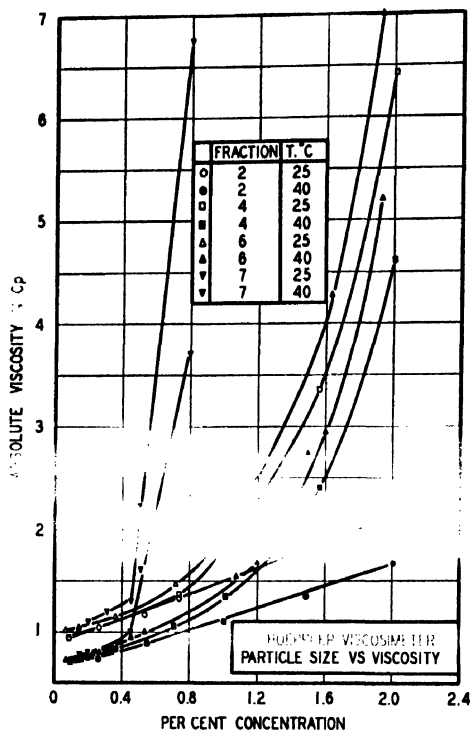


FIG. 3. Viscosities of fractions 2, 4, 6, and 7 at 25°C. and 40°C., determined in a Hoepler viscosimeter.

TABLE 8
Viscosities of fraction 2

CONCENTRATION IN PER CENT DRY WEIGHT	C_p AT 25° C.	C_p AT 40° C.
0.094	0.956	0.696
0.270	1.065	0.735
0.544	1.154	0.884
1.035	1.368	1.092
1.505	1.795	1.338
2.040	2.163	1.684

TABLE 9
Viscosities of fraction 4

CONCENTRATION IN PER CENT DRY WEIGHT	C_p AT 25° C.	C_p AT 40° C.
0.086	0.968	0.717
0.273	1.065	0.790
0.348	1.312	0.934
1.063	1.840	1.356
1.573	3.360	2.411
2.033	6.428	4.609

centration of fraction 2, the viscosity increases nearly proportionally. Only in the very high (above 2 per cent) concentrations studied does a slight deviation become noticeable.⁴ Fractions 4 and 6 deviate rapidly

⁴ The scale used in the reproduced curve does not show this deviation.

from the curve of fraction 2 above a concentration of 0.27 per cent. The increase in viscosity becomes more and more pronounced. This can be easily explained by the following considerations. The amount of particles present in a given concentration of these three different sols increases with their decreasing apparent particle diameter. The particles in sol 4 are packed closer than in sol 2, and in sol 6 closer than in sol 4. Thus the resistance against shear will increase. On this basis it is quite evident that fraction 2, having the largest particles and the smallest overall surface,

TABLE 10
Viscosities of fraction 6

CONCENTRATION IN PER CENT DRY WEIGHT	C_p AT 25° C.	C_p AT 40° C.
0.067	1.002	0.715
0.152	1.048	0.777
0.368	1.137	0.806
0.710	1.469	1.056
1.085	2.187	1.505
1.203	2.429	1.690
1.506	3.929	2.724
1.643	4.271	2.946
1.939	7.117	5.212

TABLE 11
Viscosities of fraction 7

CONCENTRATION IN PER CENT DRY WEIGHT	C_p AT 25° C.	C_p AT 40° C.
0.201	1.085	0.744
0.460	1.308	0.981
0.505	2.253	1.600
0.798	6.751	3.698
1.302		
1.409		

TABLE 12
*Viscosities of fraction 6 after
evaporation at 75°C.*

CONCENTRATION IN PER CENT DRY WEIGHT	C_p AT 25° C.	C_p AT 40° C.
0.153	1.038	0.756
0.306	1.093	0.805
1.045	1.892	1.376
1.358	2.473	1.703

TABLE 13
*Viscosities of fraction 6 after
evaporation at 95°C.*

CONCENTRATION IN PER CENT DRY WEIGHT	C_p AT 25° C.	C_p AT 40° C.
0.283	1.093	0.791
0.582	1.350	0.956
1.177	2.116	1.480

will begin to show a more rapid increase in viscosity only in concentrations very much higher than those of fractions 6 and 4.

The values obtained for the viscosity of the first two sols of fraction 7 (table 11) (the original sol and the one obtained therefrom by dilution) correspond to these considerations. The first sol of fraction 7 obtained by reconcentration shows a very sudden and enormous increase in viscosity, which could also be recorded for the second sol obtained by evaporation and which is in line with the extremely high apparent specific gravities recorded. These are the sols where, as previously mentioned, thixotropy could already be observed at concentrations as low as 1.4 per cent. If we

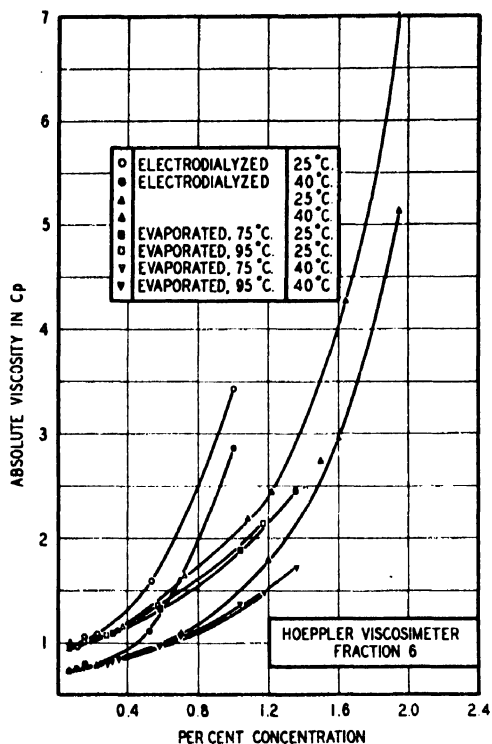


FIG. 4. Change in viscosity of fraction 6 after concentration, determined at 25°C. and at 40°C. in a Hoepler viscosimeter.

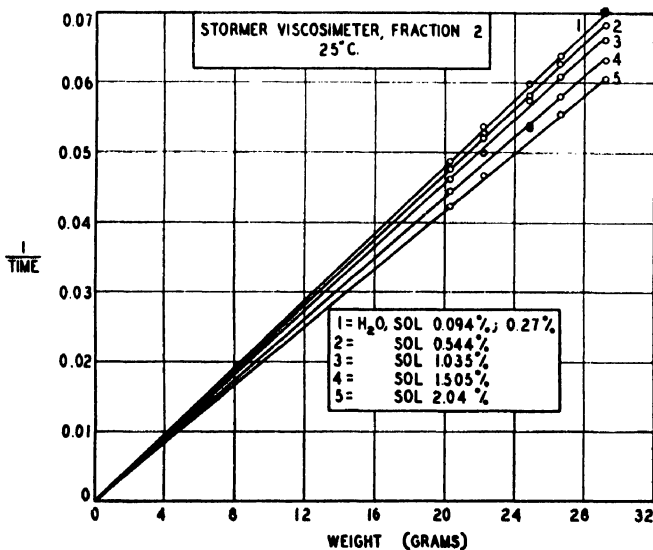


FIG. 5. Fraction 2 in a Stormer viscosimeter at 25°C.

- assume that at a given concentration the thickness of the adsorbed water layer surrounding a particle would be the same if the apparent particle

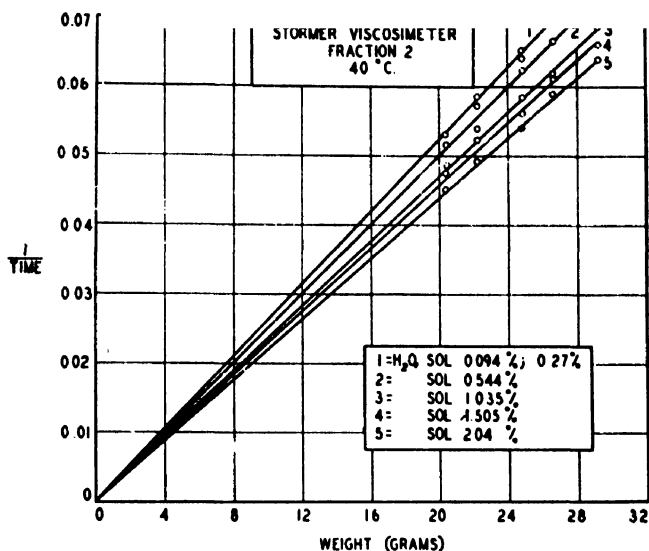


FIG. 6. Fraction 2 in a Stormer viscosimeter at 40°C.

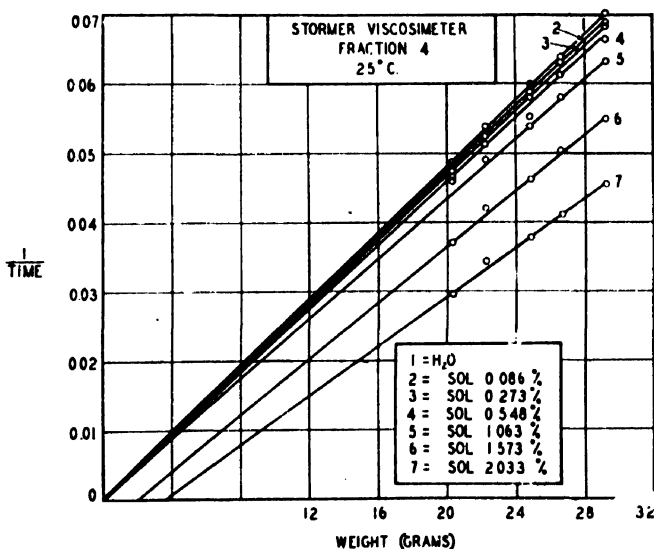


FIG. 7. Fraction 4 in a Stormer viscosimeter at 25°C.

diameter is $28\text{ m}\mu$, $14\text{ m}\mu$, or less, then the ratio of adsorbed water to particle will be greater the smaller the particle. Therefore comparatively more

water will be immobilized in a sol of extremely fine particles than in one of greater particle size.

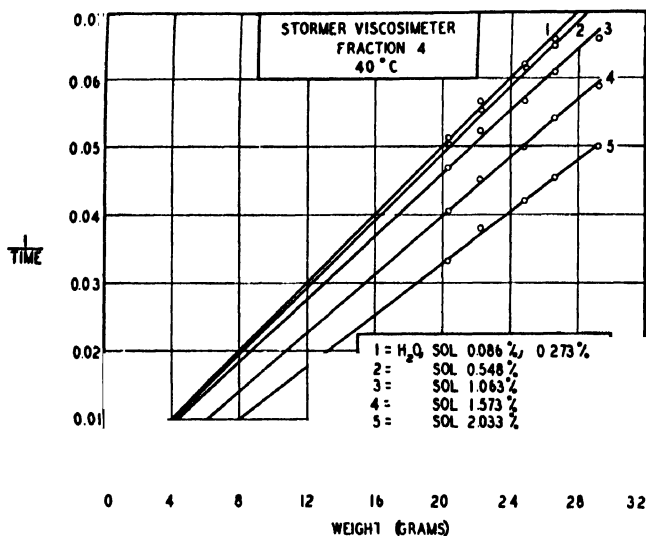


FIG. 8. Fraction 4 in a Stormer viscosimeter at 40°C.

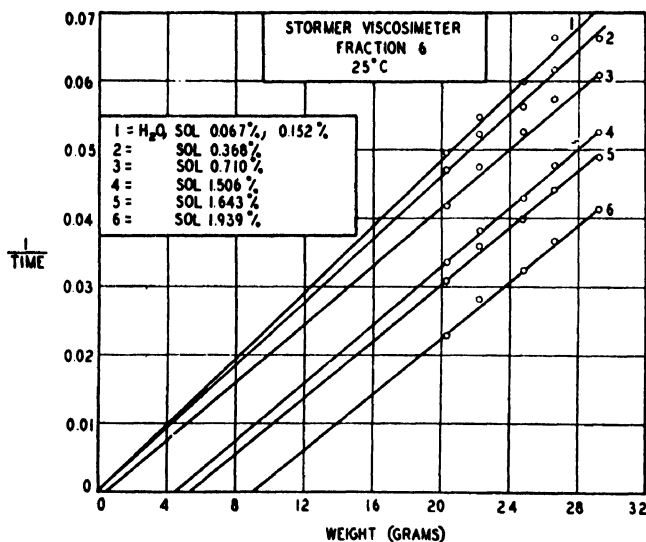


FIG. 9. Fraction 6 in a Stormer viscosimeter at 25°C.

The viscosity measurements in the Høepler viscosimeter for fractions 4, 6, and 7 were discontinued as soon as the first signs of "structural viscosity" could be detected, since in our opinion even the refined falling-ball

method cannot give accurate and reproducible results in systems of such a nature.

The viscosities of fraction 6, reconcentrated at 75°C. and 95°C., show

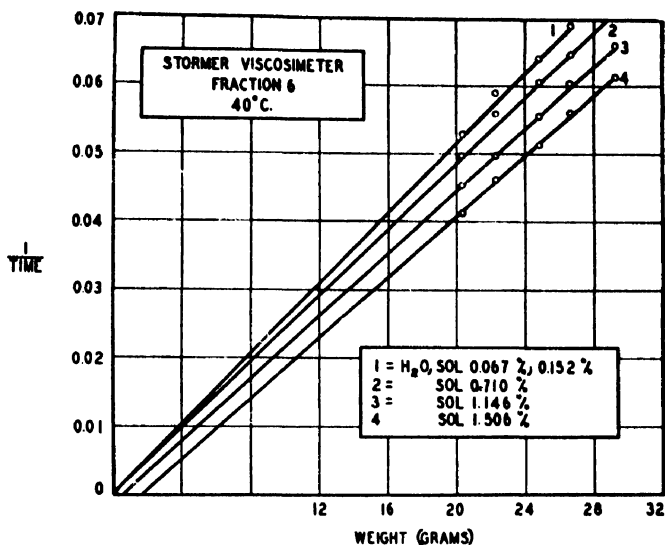


FIG. 10. Fraction 6 in a Stormer viscosimeter at 40°C.

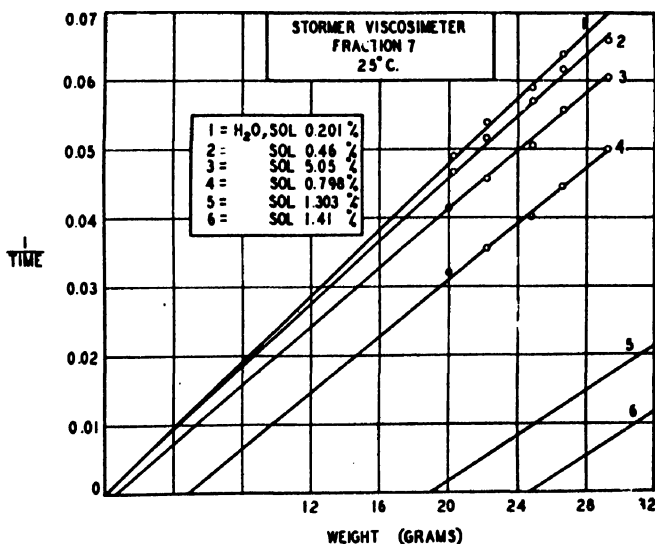


FIG. 11. Fraction 7 in a Stormer viscosimeter at 25°C.

very little change up to concentrations of 1.17 per cent (tables 12 and 13). In higher concentrations the viscosity does not rise to the same degree as the original (figure 4).

The determinations of absolute viscosity at 40°C. gave the results to be expected. A general decrease in viscosity is observed.

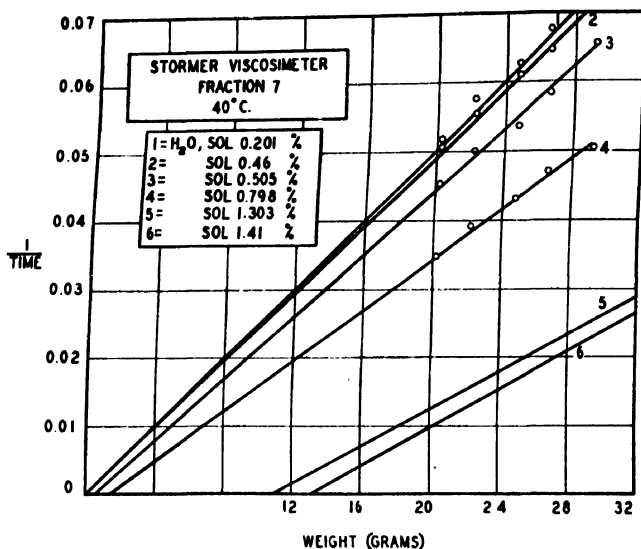


FIG. 12. Fraction 7 in a Stormer viscosimeter at 40°C.

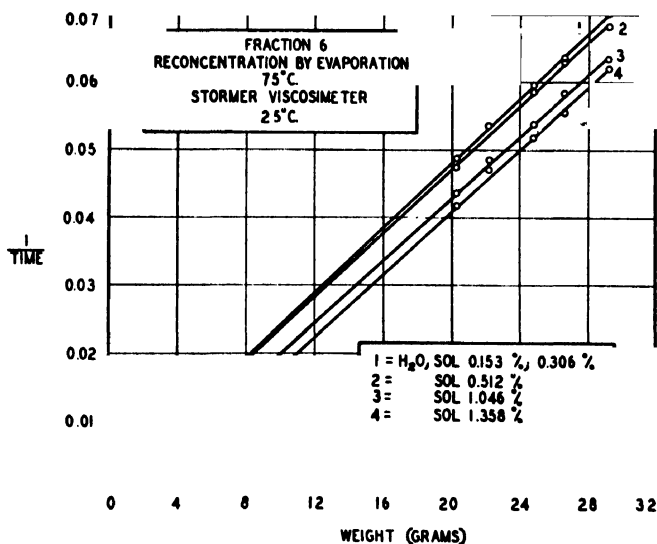


FIG. 13. Fraction 6, reconcentrated by evaporation at 75°C., in a Stormer viscosimeter at 25°C.

Since it is impossible to make any accurate statements as to the formation of a structure or the development of a yield point when using a falling-

ball type of instrument, it was decided to study the different sols in a Stormer viscosimeter at 25°C. and 40°C.

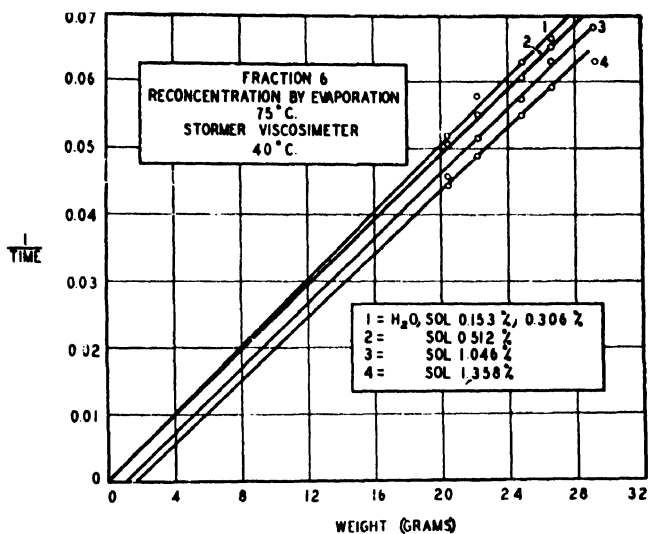


FIG. 14. Fraction 6, reconstituted by evaporation at 75°C., in a Stormer viscosimeter at 40°C.

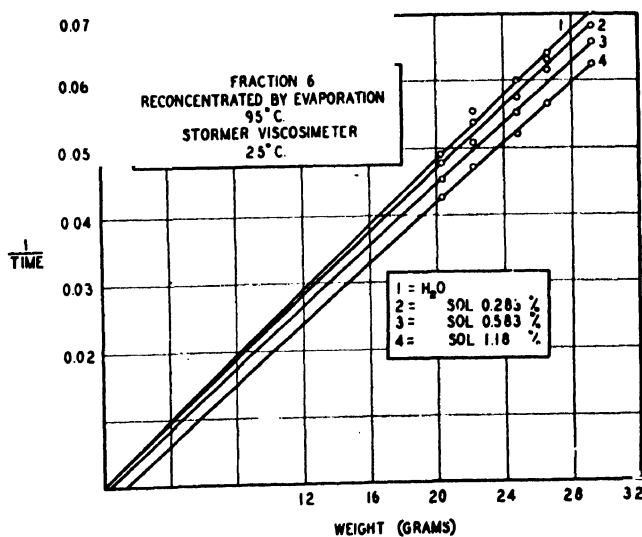


FIG. 15. Fraction 6, reconstituted by evaporation at 95°C., in a Stormer viscosimeter at 25°C.

Fraction 2, which consists of the coarsest particles (average apparent particle diameter = 48 μ), exhibits no yield point up to 2.04 per cent

(figures 5 and 6). Fraction 4 (average apparent particle diameter = $28\text{ m}\mu$) reveals a noticeable yield point at 1.5 per cent (figures 7 and 8), fraction 6 (average apparent particle diameter = $14\text{ m}\mu$) at 1 per cent (figures 9 and 10), and fraction 7 (average apparent particle diameter less than $14\text{ m}\mu$) at 0.5 per cent (figures 11 and 12). At 40°C . all the yield points decrease. The decrease becomes the more pronounced the smaller the particle sizes of the fractions studied. The yield points naturally increase with increasing concentration. No appreciable changes in yield points of fraction 6 have been found when reconcentrating the sols by evaporation (figures 13, 14, 15, 16).

The results of viscosity determinations have demonstrated that the viscosity follows the Einstein equation only for the coarsest fraction and in

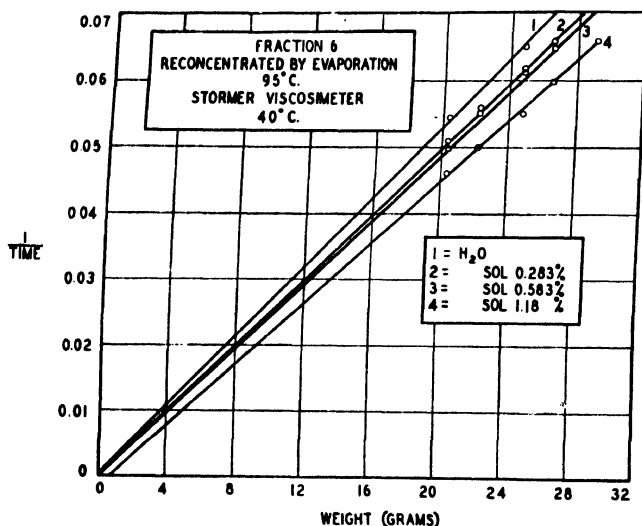


FIG. 16. Fraction 6, reconcentrated by evaporation at 95°C ., in a Stormer viscosimeter at 40°C .

extreme dilutions. For the finer particles increasing deviations are observed. Yield points also increase with decreasing particle sizes and increasing concentration. The unexpectedly high viscosities at the concentrations studied cannot be accounted for by simple particle interference. In addition a high degree of solvation (adsorbed water hulls) is necessary to explain this fact satisfactorily.

It seems only logical that such a bond will be weaker the higher the temperatures, thus causing a reduction in viscosity.

OPTICAL DENSITY

It finally was decided to examine the finest fractions for their light transmission, as it was hoped that such measurements might permit some

insight as to the actual distribution of the particles in the sols. A Hardy color analyzer (1) was used for this purpose. All measurements were recorded with distilled water as a blank.

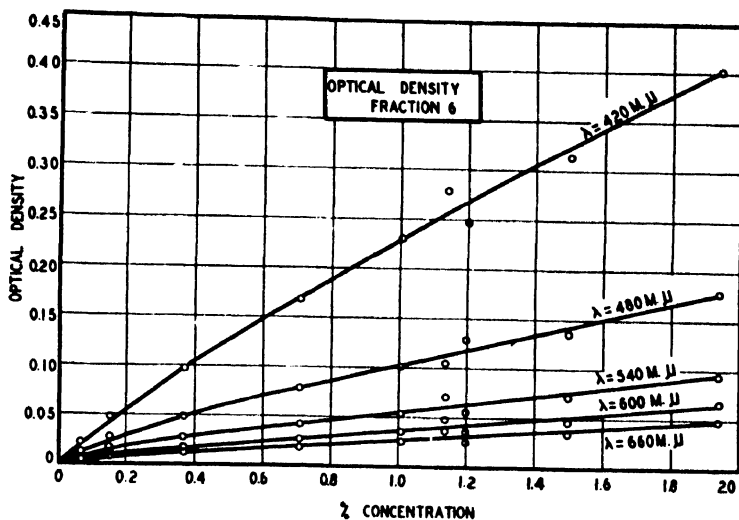


FIG. 17. Optical density of fraction 6

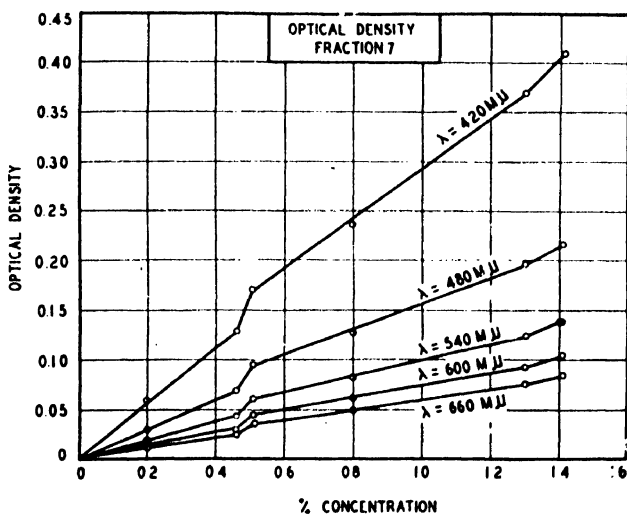


FIG. 18. Optical density of fraction 7

The curves for the optical density of fraction 6 show a very pronounced light absorption in the smaller wave lengths (figure 17). This simply proves that the sol contains a large number of small particles.

The curves for the optical density of fraction 7 (figure 18) are of interest

as they show, when the sol is reconcentrated by evaporation, a sudden increase. These systems have a very marked tendency to form thixotropic gels when being cooled down. Although no final explanation for this phenomenon can yet be offered it seems highly probable that the particles, becoming more and more locked into equilibrium positions, cause an increased absorption or scattering. (Further work to clarify this effect is in progress.)

STREAM DOUBLE REFRACTION

Stream double refraction in fine clay fractions has already been reported by Hauser and Reed (*loc. cit.*). In the present study it was noticed in fraction 6 (average apparent particle diameter = $14\text{ m}\mu$), but seemed to be a function of the concentration of this fraction, since it became noticeable only in concentrations above 1 per cent. Below this concentration no stream double refraction could be noticed, even after prolonged storage. The part of fraction 6 which had been reconcentrated by evaporation at 75°C . and 95°C . also showed stream double refraction, but only from concentrations above 1.045 and 1.177 per cent, respectively. No stream double refraction could be observed in fraction 7, either at higher concentration or after long storage.

It seems that in these systems stream double refraction is detectable with the eye only if particles of a certain range and concentration are present, since with larger particle sizes this phenomenon again becomes less pronounced. However, even the finest fraction in extreme dilution will, if put into motion and placed between crossed nicols, exhibit strong double refraction, which proves that the slightest mechanical influence causes some orientation of the submicrons present in the system. This also proves that gelation is not a result of preferential orientation of particles.

SUMMARY

The apparent specific gravities of monodisperse montmorillonite fractions of extremely low concentrations and different particle sizes show an increase with decreasing particle size and increasing concentration. This is explained by the presence of strongly adsorbed water on the surface of the particles.

Absolute viscosity determinations of the same systems demonstrate an increase with decreasing particle size and increasing concentration. These results are in line with the changes in apparent specific gravity. The coarsest fractions show no yield point up to concentrations of 2 per cent. The finer fractions reveal an increase with decreasing particle size and increasing concentration. The yield point as well as the viscosity de-

creases with increasing temperature. Gelation seems to cause a sudden rise in optical density over all wave lengths.

Preliminary studies in stream double refraction indicate it to be a function of particle size and concentration. Orientation of the submicrons in a sol, if placed between crossed nicols, is detectable only if the system is put in motion.

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THE STRUCTURE OF THE SURFACES OF SOLUTIONS AS SHOWN BY THEIR RESISTANCE TO THE SPREADING OF INSOLUBLE FILMS¹

T. FOSTER FORD² AND DONALD A. WILSON³

Department of Chemistry, Stanford University, California

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Our knowledge of the surfaces of liquids has been derived mostly from the work of Langmuir and others on the phenomena presented by insoluble films on water. It has been commonly taken for granted that somewhat similar layers must exist upon the surfaces of solutions of all surface-active substances, even soluble substances. This assumption is based upon analogy, and upon the Gibbs prediction of positive adsorption with lowered surface tension. Elsewhere the authors have presented direct and indirect evidence for the existence of such soluble films (11, 10, 3, 4). This paper has to do with their direct quantitative study.

In these experiments the surfaces of solutions of hydrocinnamic acid, caprylic acid, and phenol are compressed by means of oleic acid "piston films," an adaptation of the recent method of Langmuir and Blodgett (1) for studying insoluble monolayers. Here the only films possible are those formed spontaneously by adsorption from the solutions themselves. The piston films are visibly retarded, and from curves showing compression against time, recorded by moving pictures, the properties of the soluble films compressed are deduced. These seem to be capable of existing in all the states of aggregation common to insoluble films. The actual amounts of solute in these soluble surface layers is found to agree quite closely with values for the absolute adsorption found by other experimental methods (4, 5, 6, 9), and with the adsorption predicted by the Gibbs equation.

THE EXPERIMENTAL METHOD

The apparatus used is shown in figure 1. It consists of a circular dish 25 cm. in diameter for containing the solution, in an air-tight glass box, with a capillary tube reaching to the center of the dish through which the

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² Present address: Shell Development Company, Emeryville, California.

³ Present address: Department of Physiological Chemistry, School of Medicine, University of Pittsburgh, Pittsburgh, Pennsylvania.

oleic acid may be introduced beneath the surface of the solution when desired. The dish is a brass hoop, paraffin waxed, fitted over a glass disk beneath which is a film of paraffin wax colored with lamp black to aid visibility. The interior of the apparatus is thoroughly paraffined to prevent contamination. The motion picture camera, not shown in figure 1, was mounted directly above the spreading film. The temperature was 11°C . in all cases.

In each experiment dish and capillary were first thoroughly cleaned and rinsed with conductivity water. The solution was then put into the dish, the surface swept with paper strips, and the enclosure covered for the

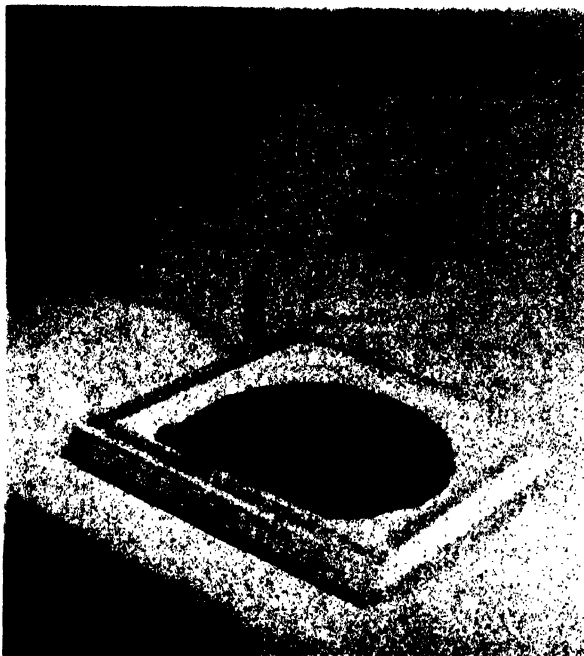


FIG. 1. The spreading-film apparatus

desired length of time. The spreading oil was introduced by trapping a droplet from an eye-dropper in a column of solution in the vertical part of the capillary tube outside the enclosure so that solution and spreading oil ran into the dish by gravity. Before introducing the spreading oil, the cover was lifted just long enough to dust the surface of the solution with talc. All the necessary data were taken from the motion picture record by projecting successive frames onto a screen.

THE SPREADING OF OLEIC ACID ON WATER

The behavior of the oleic acid piston when compressing the surface of pure water is shown by the first compression curves in figures 3, 4, 5, and 6.

After a very short time the rate of spreading of the film in square centimeters per exposure is constant. That is, the area-time curve becomes a straight line, and, on water, it remains a straight line during the whole time of spreading. Evidently no sensible change in the retarding force due to water alone occurs as its free surface is reduced. Changes observed on solutions, then, must be due to the presence of solute films.

The rate of disentanglement

On water the area-time curve is linear over most of its length, and on solutions large linear segments are observed. This constant rate of increase of area of the piston film is probably determined by the rate of "disentanglement" of oleic acid molecules from a central globule of quite constant size. For solid nuclei of spreading Cary and Rideal (2) found the rate of spreading, or of disentanglement, to be proportional to the perimeter of the solid at the plane of contact with the water surface. For liquid globules also they consider it probable that solution occurs only at the circumference of contact.

Oleic acid droplets released beneath water surfaces seem to form first single lenses which then suddenly break up into many smaller ones. This behavior was noted by Cary and Rideal in studying the spreading of oleic acid over very large surfaces of water, and it explains the gradual increase in the spreading rate shown by their data, since there was an increase in the total perimeter of the reservoir. On some of our concentrated solutions, on which spreading was comparatively slow, an upward swing of the area-time curves similar to Cary and Rideal's is noted. In most cases, however, on the small areas studied by us the central globule evidently did not have time to break up. Its exact behavior fortunately has little bearing on the interpretation of our results. It may only be concluded that in the first part of the spreading on solutions the rate is dependent more on the nature of the reservoir than on the properties of the surface being compressed.

The terminal linear velocity

The data given here for both water and solutions show at the beginning of the spreading a constant linear velocity of the advancing edge. This must represent a terminal linear velocity. At this speed the resistance offered by the friction in the film and underneath the film, and by impact with chance obstructions ahead of the film, must equal the spreading pressure. This terminal velocity is observed only at first, because only then is the reservoir in effect infinite. As the film increases in area the rate of spreading quickly becomes limited by the rate of disentanglement.

THE RESULTS OF THE COMPRESSION OF SOLUBLE FILMS

Typical curves for the compression of soluble films by the oleic acid piston are shown in figure 2. The actual data obtained with various solu-

tions of hydrocinnamic acid, caprylic acid, and phenol are recorded in figures 3, 4, 5, and 6. Many of the actual curves exhibit all of the characteristics formalized by the different segments in figure 2.

Terminal linear velocity

At the beginning of the compression the linear velocity of the advancing edge of the piston film is constant. This is the terminal velocity discussed above.

On a few of the more concentrated solutions the data suggest a slight acceleration of the linear velocity near the origin. Such an effect could

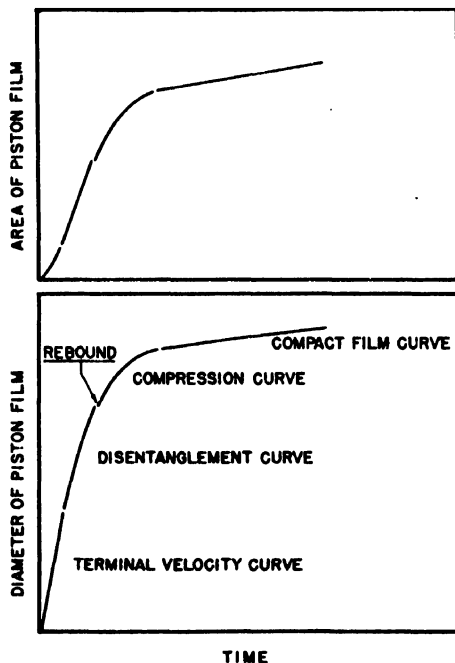


FIG. 2. Typical compression curves for soluble films

result from the fountain-like manner in which the oleic acid is introduced into the surface, since a certain time should be required for the formation of a lens having a stable perimeter. The necessity of accelerating the talc particles used for reference may also be a factor. In most cases these effects are masked in our experiments by attainment of the terminal velocity in less than the 0.076 sec. elapsed between successive camera exposures.

Disentanglement

On almost all of the compression curves for soluble films a point is reached beyond which the area-time curve rather than the diameter-time

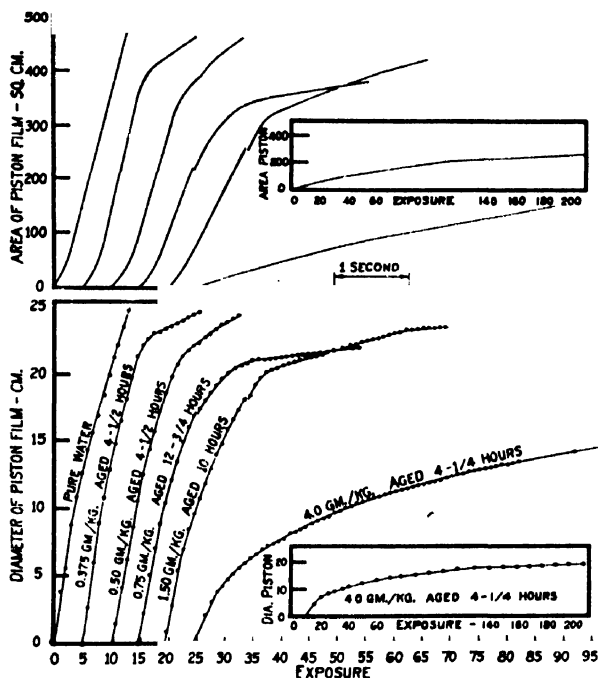


FIG. 3. Compression curves for aged surfaces of hydrocinnamic acid solutions

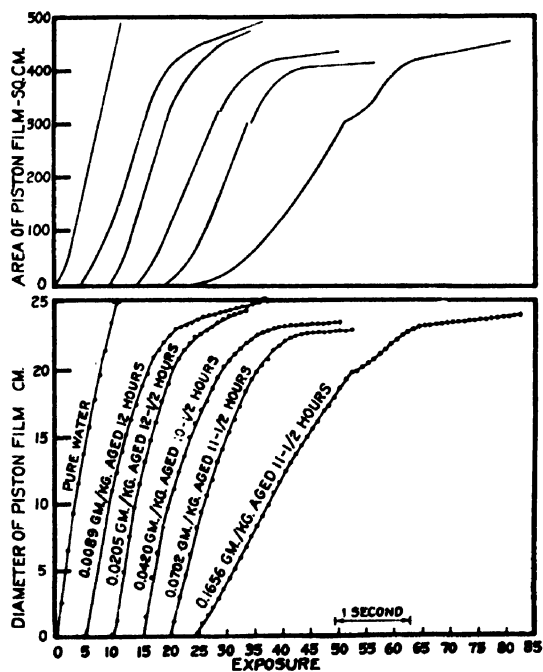


FIG. 4. Compression curves for aged surfaces of caprylic acid solutions

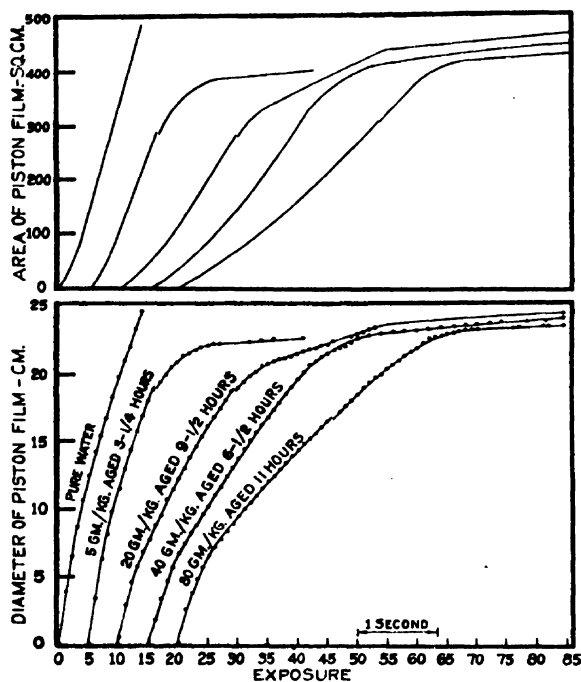


FIG. 5. Compression curves for aged surfaces of phenol solutions

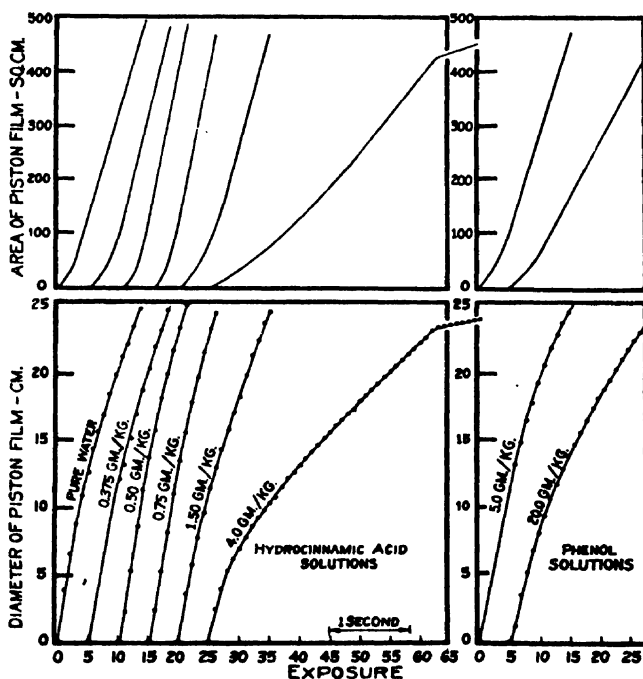


FIG. 6. Compression curves for freshly swept surfaces

curve becomes a straight line. It has been assumed that at this point the spreading rate becomes limited no longer by the terminal velocity but by the rate of disentanglement of molecules from the central globule.

If the rate of disentanglement is assumed to be proportional to a difference in spreading pressure between the piston film and the film compressed, then the soluble film must oppose the piston film with a constant pressure in the region where the area-time curve is linear. This portion of the curves, then, may be assumed to represent a transition from one surface phase to another. Presumably this change is from the two-dimensional gaseous state to a two-dimensional liquid state, a presumption confirmed by the nature of the subsequent changes.

If the central globule always had the same perimeter on the different solutions, then the slopes of the disentanglement curves should be expected to be the same on solutions of the same solute regardless of concentration if two-dimensional condensation were occurring, and on solutions of different solutes the slopes should be proportional to the two-dimensional vapor pressures of the solutes.

It seems probable, however, that the perimeter of the central globule should itself be a function of the initial opposing pressure, as well as of the vapor pressure, and the slopes of the disentanglement curves should tend to decrease with increasing concentrations of solutions, as observed.

Rebound compression of the piston film

Immediately after or during the period of disentanglement, most of the curves show a momentary break in the progress of the piston film. In slow motion the films seem actually to stand still for an instant. A possible explanation is that at this point the piston film, which has been in the so-called liquid expanded state, is opposed by a force sufficient to compress it to a more compact form. At the same time the soluble film may or may not be undergoing compression. When the piston film has been compacted, the normal compression of the soluble film proceeds.

From the existence of the "rebound" it is reasonable to suppose that until compression to this point the soluble film was in some state more expanded than that of the piston film. That the point of rebound coincides roughly with the departure of the area-time curve from linearity would confirm the presumption that this point marks the completion of a transition from the gaseous to the liquid state. Another alternative explanation, depending upon the momentum of the body of the liquid set in motion toward the walls of the containing vessel by the advancing film during the period of its fastest motion, has been mentioned elsewhere (7).

The change from liquid to compact films

The rounded portions of the curves, where neither the area nor the diameter is a linear function, apparently represent compression of the

"liquid" films to compact films. The compression of the compact films, in which the rate of reduction in area is comparatively low and may be assumed to depend only on the rate of escape of molecules from the films, is represented by the final linear or approximately linear portions of the curves.

By extrapolating these final linear portions of the curves backward we presumably obtain the total areas that all of the molecules in the soluble films at any time would occupy if compressed into films as closely compacted as these curves represent. In table 1 these minimum compact film areas are compared to the actual areas of the films for the particular point

TABLE 1

Ratios of horizontal cross sections, A_h , to vertical cross sections, A_v , of molecules as deduced from film experiments and as calculated from data from other sources

SOLUTION	CONCENTRATION	AGED	A_h/A_v (FILM EXPERIMENTS)	A_h/A_v (CALCULATED)
	grams per kilo-gram	hours		
Hydrocinnamic acid	0.375	4½	1.27	1.6
	0.5	4½	1.38	1.6
	0.75	12½	1.60	1.6
	1.5	16	1.43	1.6
	4.0	4½	1.56	1.6
Caprylic acid	0.0089	12	1.88	2.4
	0.0205	12½	1.89	2.4
	0.0420	10½	1.89	2.4
	0.0702	11½	1.95	2.4
	0.1656	11½	1.86	2.4
Phenol	5.0	3½	1.7	1.4
	20.0	9½	1.2	1.4
	40.0	6½	2.0	1.4
	80.0	11	1.5	1.4

where the disentanglement curves cease to be linear. The ratios are seen to agree very well with the ratios between the vertical and horizontal cross sections of the molecules, as calculated from x-ray data or as deduced by analogy with data for insoluble films. From the apparently real discrepancy in the case of caprylic acid it may be concluded that many of these molecules already are oriented in the uncompressed surfaces. The conclusion from these results is that in the transition from the liquid to compact films the essential change is in the "up-ending" of molecules in the surface.

These results confirm the original presumption that, in the compression of soluble films as well of insoluble films, the transitions are from the

two-dimensional gaseous state, to the liquid state, to a solid or compact film state.

Adsorption accounted for by the surface films

If extrapolating the compact film curves back to zero time gives the total areas which could have been occupied by all the molecules in the original soluble films, if compacted, then in each case the number of grams of solute originally present as a film per square centimeter of surface can

TABLE 2

Values of adsorption for hydrocinnamic acid, caprylic acid, and phenol solutions as obtained from the areas of the compact solute films at 11°C. and as calculated from surface tensions at ordinary temperatures

SOLUTION	CONCENTRATION	AGED	$\Gamma \times 10^3$ G. PER CM. ²	
			Extrapolated compact films	Calculated from surface tension data
	grams per kilogram	hours		
Hydrocinnamic acid	0.375	4½		1.7*
	0.5	4½		2.0*
	0.75	12½	3.7	3.2*
	1.5	16	4.3	5.2*
	4.0	4½	6.4	7.6*
Caprylic acid	0.0089	12		1.1†
	0.0205	12½		2.2†
	0.0420	10½	2.8	3.7†
	0.0702	11½	3.0	5.5†
	0.1656	11½	4.0	7.8†
Phenol	5	3½	1.9	2.1† 2.0†
	20	9½	1.3	4.2† 4.2†
	40	6½	1.3	4.4† 4.3†
	80	11	1.3	4.4† 2.3†

* Bacon and Swain, unpublished results.

† D. A. Wilson, unpublished results.

‡ From data of Harkins and Grafton (J. Am. Chem. Soc. 47, 1329 (1925)).

be calculated by assuming that the area per molecule in the film is the same as the vertical cross-sectional area of the molecules as calculated from x-ray data. The results represent the amount of the Gibbs adsorption which is accounted for as existing in the surface as a film, in these cases. In table 2 these values are compared with the theoretical values of adsorption as calculated from surface tensions. The failure of the calculated adsorption to be wholly accounted for by the film measurements in every case might arise from a greater rate of escape of molecules from gas-

eous and liquid films than from compact films, which would cause the areas of compact films found by back extrapolation to be lower than the true areas.

It can be concluded from these results that the adsorption predicted from the lowering of surface tension with increasing concentration is at least largely accounted for by the existence of a soluble film in the surface. By the microtome method and by interferometric methods it appears to have already been shown, at least for the case of hydrocinnamic acid (6, 9, 5), that the total amount of adsorption in a surface at equilibrium is in practical agreement with that predicted from the lowering of the surface tension. Apparently, then, the adsorption exists in the surface substantially as a soluble film, and there is here no evidence for a concentration gradient into the body of the solution at equilibrium.

THE COMPRESSION OF FRESHLY SWEEPED SURFACES

Compression curves for freshly swept surfaces are shown in figure 6. Except on the most concentrated solutions, the behavior of the piston film is seen to be practically the same as on pure water. Each surface was carefully swept several times with paper strips, by the same procedure as used in cleaning all the surfaces before beginning an experiment. By "freshly swept" is meant that the time allowed for aging after sweeping was between 30 sec. and 2 min. From the results the conclusion might be drawn that the sweeping effectively removes any soluble as well as any insoluble film which may be on the surface, for the freshly swept surface appears to be almost identical with a pure water surface on dilute solutions and to carry only an attenuated gaseous film on concentrated solutions.

This result also is at least superficially in agreement with experiments by the microtome method (4, 6). There it was found that the absolute adsorption of hydrocinnamic acid reached the true equilibrium value only after about 12 hr., and that when only a few minutes were allowed with this apparatus the observed adsorption was much reduced. However, a film could appear in the surface almost instantaneously by denudation of the underlying layers of solution and the microtome would not detect it, because this apparatus removes an average sample, including both film and denuded layers (8).

The present experiments show either that there is no film on a freshly swept solution or that it is so readily displaced into the layers immediately beneath the surface as to offer no appreciable resistance to the motion of the oleic acid piston. It is difficult to believe that there is no film upon or in the surface, because the surface tensions of freshly formed droplets are found to be already greatly reduced, and it is indeed from drop-weight surface tensions that we calculate the theoretical values of the absolute adsorption which the microtome and other methods confirm. It seems

possible, however, that in our experiments, where the surfaces were repeatedly swept with absorbent paper strips, the solute might have been almost completely removed from the surface layers by the sweeping, so that the spreading actually occurred, in effect, on greatly diluted surfaces. For formation of a film corresponding to the Gibbs adsorption on a 1.5 g. per kilogram hydrocinnamic acid solution total denudation to a depth of 3500 Å. would be necessary. This great depth of denudation might be used to support the alternative assumption that the film exists but is readily displaced, because in the layers immediately under the film there are no solute molecules tending to replace those escaping from it. These points should be settled by measurements of surface tensions on freshly swept solutions, which are now in progress in this laboratory.

SUMMARY

1. A new technique for the investigation of soluble films of positively adsorbed solutes upon the surfaces of their solutions has been developed.
2. Films of solute molecules have been shown to exist upon aged surfaces of solutions of caprylic acid, hydrocinnamic acid, and phenol, whereas the surfaces of freshly swept solutions seem more nearly to resemble water.
3. The analogy between these films of adsorbed solute molecules and two-dimensional insoluble films has been demonstrated.
4. The amount of solute in these soluble films is found to be of the same order of magnitude as predicted by the Gibbs theorem.

The authors wish to express their thanks to Professor J. W. McBain for the interest he has taken in this work.

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OPAQUE ULTRACENTRIFUGES FOR DIRECT ANALYSIS^{1,2}

JAMES W. McBAIN

Department of Chemistry, Stanford University, California

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Upon a recent occasion Kracmer (6) stated that nowadays the first instrument which any colloid laboratory should acquire is an ultracentrifuge. This must have seemed to many listeners and readers a counsel of perfection unattainable without special financial resources. It is the purpose of this presentation before the Colloid Symposium to exhibit some of the inexpensive alternatives which are now available to any scientific laboratory that has only modest means, but yet is not satisfied with anything less than the highest degree of accuracy so far attained in this field.

The opaque ultracentrifuges³ designed and developed by the author and his collaborators at Stanford University are all based on the direct air-driven spinning top of Henriot and Huguenard (5). They possess no optical system, and they are run at any desired constant temperature, in the open air (not *in vacuo*), the driving air being passed through a coil of copper pipe immersed in a thermostat. They run at 125,000 to 156,000 R.P.M. with an air pressure of 100 lb. per square inch, but lower pressures of air are usually employed. The steel must be protected with many thin coats of Bakelite lacquer, each baked on at 135°C.

With these simplest of means, both sedimentation velocity and sedimentation equilibrium are readily measurable with great accuracy. The sedimentation equilibrium of sucrose (9) yielded a molecular weight of 341 instead of the theoretical value 342. The sedimentation velocity of egg albumin (7) measured in rotor V (described below) gave $s_{20}^{\circ} = 3.56 \times 10^{-13}$

¹ Presented at the Fifteenth Colloid Symposium held at Cambridge, Massachusetts, June 9-11, 1938.

² Transparent ultracentrifuges are not discussed here, but it may be mentioned that the original air-driven ultracentrifuge of McBain and O'Sullivan (*J. Am. Chem. Soc.* **57**, 780, 2631 (1938)) has been so improved that it is available for every purpose; for example, the sedimentation velocity of hemoglobin was found by A. H. Lewis to be $s_{20}^{\circ} = 4.65 \times 10^{-13}$, in agreement with the value 4.63×10^{-13} published by Steinhart (*J. Biol. Chem.* **123**, 543 (1938)), rather than the previous value of 4.5×10^{-13} obtained at the University of Upsala.

³ Eight different designs of these ultracentrifuges were exhibited at the Colloid Symposium, in addition to the transparent rotor of McBain and O'Sullivan. The external diameter of the rotors was usually 37 mm.

in good agreement with the definitive value 3.55×10^{-13} published by workers at the University of Upsala.

An ultracentrifuge avoids convection in the sedimenting liquid. This is achieved either by careful avoidance of temperature fluctuations and of vibration, or by allowing the sedimentation to take place within narrow radial spaces mechanically shielded from convection. With the direct air-drive we employ, the temperature is as constant and fixed as the thermostat.

I. PRIMITIVE ONE-PIECE ROTOR

We may begin with a reference to the very simplest hollow one-piece rotor with which many problems can be solved. The system may be immobilized by the use of a jelly or curd, the method introduced by McBain and Stuewer (8). This enables the sedimentation equilibrium of any substance present to be measured, but it is unsuitable for the measurement of sedimentation velocity except that of the jelly structure itself. With 0.3 per cent agar jelly it gave the same sedimentation rate (65×10^{-13}) as was given (63×10^{-13}) by the transparent ultracentrifuge of McBain and O'Sullivan. Swelling pressures of the jellies were also measured.⁴ Soap curd was used in the sedimentation equilibrium of sucrose (9). Details and drawings of the one-piece top may be found in earlier articles (8, 9).

II. ROTOR WITH ANNULAR WASHERS FOR SEDIMENTATION EQUILIBRIUM

In this rotor, fully described by McBain and Tostado (9), the immobilized sedimenting liquid lies between horizontal annular washers spaced at uniform known distances apart by using alternately narrow and wide washers. Convection is permitted in the liquid in contact and in equilibrium with the innermost part of the sedimentation column. Analysis of this liquid before and after gives the molecular weight of any monodisperse substance, such as sucrose, or larger particles.

⁴ Dilute agar jelly has been used in the National Institute for Medical Research, London (Schlesinger: *Nature* **138**, 549 (1936); Schlesinger and Galloway: *J. Hyg.* **37**, 445, 463 (1937)) to convert the Sharples Super-Centrifuge into a convectionless ultracentrifuge. Five cubic centimeters of virus solution gelatinized with dilute agar lines the closed bowl to a depth of 0.18 mm. Another 5 cc. is then added and the film is so thin that convection does not occur, thus allowing both rate and equilibrium to be measured. Virus of foot-and-mouth disease is measured after 3 min. An antibody required only 30 min. for sedimentation equilibrium. It is necessarily assumed that the agar jelly is of such concentration that it neither swells nor sediments. This, however, can be verified by direct experiment and adjusting the concentration of agar to the requisite value. Any influence of the agar on the absolute rate has to be tested by comparison in some other ultracentrifuge. Sedimentation equilibrium is of course unaffected (McBain: *Science* **87**, 2250 (1938)).

III. ROTOR WITH ANNULAR WASHERS FOR SEDIMENTATION EQUILIBRIUM

This insertion in a rotor, designed by Tostado, is a modification of rotor II, permitting analysis of the liquid above and below the sedimenting column, especially for use in polydisperse systems. Here the annular washers are all alike and are merely piled loosely upon each other. They are kept centered by perforated buttresses or bosses on the container, as

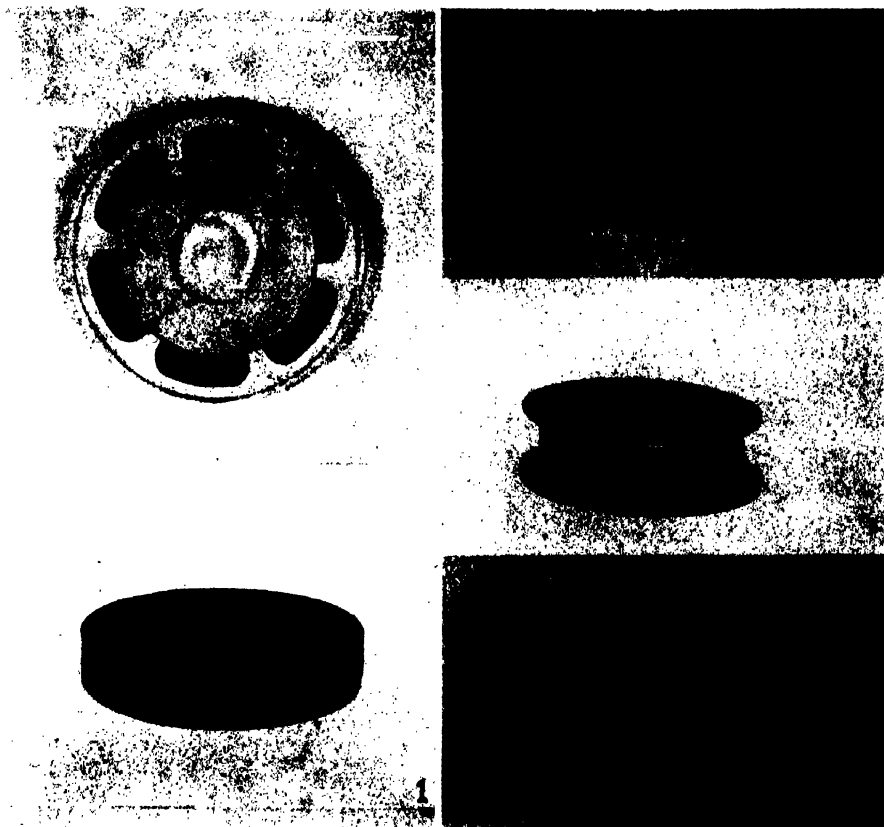


FIG. 1. Rotor with annular washers for sedimentation equilibrium

FIG. 2. Rotor for sedimentation velocity or equilibrium using solid circular discs

is shown in figure 1. The liquid from the middle and the exterior has to be withdrawn at approximately the same rate to avoid mixing. In using rotors II, III, IV, V, and VII the rotor is stopped before analysis, and experience shows that this is easily accomplished without mixing. With rotor VI the samples must be taken while running; in the case of rotor I this is merely a matter of optional convenience, using the technique described elsewhere (8, 9).

IV. CONCENTRIC BAFFLE RINGS FOR ANALYSES OF THE DIFFERENT FRACTIONS OF THE SEDIMENTATION COLUMN

In certain cases such as the soaps it is advisable to analyze all portions of the sedimenting column. The method suggested by my former collaborator, Dr. Tirey Foster Ford,⁵ is to use concentric metal rings closely fitting and bored radially with numerous holes. Our own method, also exhibited, is to use instead concentric piles or nests of loosely piled washers, each pile being held as a unit by three vertical pins connecting the uppermost and lowermost washer of that set. This has the advantage of providing radial spaces for sedimentation.

V. ROTOR FOR SEDIMENTATION VELOCITY OR EQUILIBRIUM USING SOLID CIRCULAR DISCS

The simplest and for most purposes the best design (7) is that of McBain and Leyda (figure 2). The cells are ideally radial, consisting of a central pile of discs about 0.08 mm. thick, alternately wide and narrow, with a larger disc just fitting the container at top and bottom to keep them central. A vertical axial pin runs through the central solid pile of metal, holding it together. The sedimenting liquid is immobilized between the successive larger discs. Both the liquid outside the discs and that within them is analyzed. About 2.2 cc. of liquid has been employed.

Polydisperse systems require that runs be made at several speeds. There is also the advantage that every constituent may be analyzed for independently. Such opaque ultracentrifuges possess the further advantage over any transparent ultracentrifuge that the whole of the column of liquid from its upper surface outwards and from the very beginning of the sedimentation is available, without distortion, for exact measurement. Incidentally, the agreement of the measurements of sedimentation velocity made with this cell with those obtained by the McBain and O'Sullivan transparent ultracentrifuge and those of Svedberg shows that there is no wall effect upon velocity of sedimentation or diffusion where the spaces are as small as 0.08 mm., as would indeed be expected from hydrodynamic theory. The protein particles or molecules are 10,000 times smaller than the capillary spaces. Recently Svedberg and his collaborators (14) have been making effective use of a similar analytical method by putting a partition of filter paper in the middle of their transparent ultracentrifuge cell.

Attention is also directed to the design of the rotor by which a perfectly tight seal has invariably been obtained. The lower part of the rotor, ruggedly made of 4 UMA steel, has placed upon it in succession a narrow loose washer to cause slipping when assembling, a thin metal disc, a disc

⁵ Present address: Shell Development Company, Emeryville, California.

of thin rubber or Pliofilm, or rubberized Cellophane, etc., and upon this the upper part of the rotor is directly screwed down. Its thinner longer annular wall bends outwards in the centrifugal field, engaging still more tightly in the lower piece. The rotor is assembled and opened upside down so as not to disturb the cell and its contents. Two small nicks are made in the periphery of the cell to enable the liquid to be withdrawn before taking out the cell if desired.

VI. ONE-PIECE STEEL ROTOR WITH WINDOW AND WITH SECTORIAL BAFFLES

When it is inconvenient to make a two-piece rotor, or where with a non-aqueous solvent a suitable seal cannot readily be found, the simplest one-piece rotor (as in I) may be used for sedimentation equilibrium (as in II) by simply inserting sectorial baffles (cut radially from annular

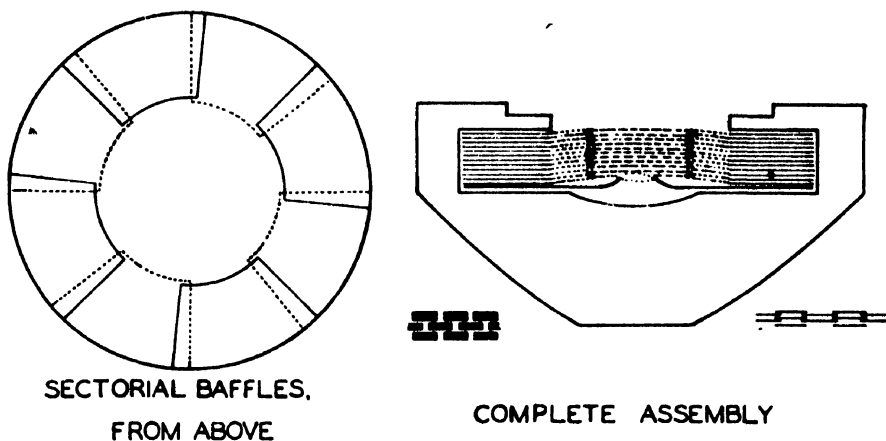


FIG. 3. One-piece steel rotor with window and with sectorial baffles

washers) piled like open brickwork. For sedimentation velocity it is necessary first to place in the rotor a circular distributing disc. When platinum is used for this purpose the rotor must not be more than 20 mm. in diameter, since larger pieces of such pure soft metals as silver and platinum flow freely in the centrifugal field. In a two-piece rotor any strong metal or plastic may be used. A window must be left in the upper part of the two-piece rotor. The platinum disc is inserted in the one-piece 20-mm. rotor folded like an umbrella and then opened out. Through its center there is a smooth hole with upturned edges. Upon the distributing disc is piled the annular circle of sectorial baffles (figure 3).

To make a measurement of sedimentation velocity, only sufficient liquid is put in to fill the spaces between the baffles. After the top has been spinning for a suitable time, the Cellophane window is opened with a flame or

a razor (8, 9) without stopping the rotor. Then a heavy liquid such as carbon tetrachloride is inserted through the hole in the platinum, which instantly distributes it outside all the baffles, displacing an equal volume of liquid inwards. This is collected with a glass capillary scraping pipet. When a colored material is sedimenting, such as the respiratory protein of earthworm blood, no precautions whatever are taken except to stop when the pipet begins to collect some colored liquid. The sedimentation velocity obtained is naturally too large. In the case of earthworm blood such crude measurements (even with thick baffles) yield values of 80 to 90×10^{-13} instead of Svedberg's value of 61×10^{-13} . However, even an approximate analysis as by color, or color reaction etc., enables correction to be made to the actual distance the meniscus has sedimented, the total volume displaced being known from the carbon tetrachloride added. Method VI is far inferior to V when thick baffles with essentially liquid only between their edges are employed, but with thin baffles, as in II to V, placed just so as just to overlap, it is much improved and contains much more liquid.

VII. A LARGER ROTOR WITHIN INVERTED IMMERSED METAL TUBES FOR VELOCITY OR EQUILIBRIUM

This is a modification by a number of workers at Stanford University of the idea first employed by Elford and his collaborators (2, 3, 4, 13) and of the rotor of McIntosh and Selby (10, 11).

VIII. FORD'S MODIFICATION FOR GLASS CAPILLARY TUBES

The lower part of the rotor has a flat cylindrical depression upon its upper surface. In this rests a thin tray carrying two circular flanges through which holes are bored radially. Through these are placed glass capillary tubes closed at the outer end. The tray is held down by a broad-headed screw. This is suitable for velocity using Elford's method of observing the position of the boundary after the rotor is stopped, either by eye, using the color or scattered light or fluorescent light or cutting the tube in two for analysis, or by photography along with a series of tubes of different concentrations. This latter method has also been used by Dr. Ford for observing sedimentation equilibrium of hemolyzed beef blood.

IX. THE BECHHOLD-SCHLESINGER CONVECTIVE PROCEDURE

This method was originated (1, 12) in 1931. It encourages slow convection. Originally a commercial centrifuge was used. During the following years various quantitative and semiquantitative observations of its occurrence were made in the author's laboratory at Stanford, in that of Beams at Virginia, and also by Gratia in Belgium, using the simplest form of the one-piece hollow rotor I. Although admitting of quantitative results this

is not an ultracentrifuge, and the periphery must be of, or lined with, some material which like filter paper holds all particles sedimented into it. McIntosh and Selby (10, 11) obtained quantitative results for the sedimentation velocity of bacteria, viruses, phages, and oxyhemoglobin, and also measured the actual specific gravity of the sedimenting particles. For example, McIntosh and Selby obtained a diameter of 56 Å. for oxyhemoglobin, identical with that quoted by Svedberg.

Where in the absence of convection the concentration of the homogeneous part of the liquid after time T would become proportional to $R(1 - e^{-\kappa T})$, where R is the radius, Bechhold and Schlesinger have shown that with convection it will be proportional to $h(1 - e^{-\frac{R}{h} \cdot \kappa T})$, where h is the inner radius of the sedimenting liquid. But after a given time in an ultracentrifuge, all the particles will have been centrifuged out, whereas in the centrifuge the concentration is asymptotically impoverished. Bechhold and Schlesinger show that therefore, if the centrifuging is greatly prolonged, the residual concentration of the convecting liquid becomes exceedingly sensitive to the size of the sedimenting particles, a change of twice the diameter soon making a difference of 10^5 -fold in the concentration or as much more as is desired. This is valuable with virus or phage where the analysis may be good only to a single power of 10.

In conclusion, it may be noted that even the Bechhold Schlesinger method may be used for distinguishing between monodisperse and multidisperse systems. It is easy to ascertain whether or not two substances are combined or associated with each other or sediment separately (as was done, for example, by Gratia in 1934).

It is evident that the problem of obtaining exact quantitative data on sedimentation velocity, sedimentation equilibrium, the actual density or the true partial specific volume has been completely solved by simple means within the reach of every scientific laboratory, and that the time is approaching for this to be a routine experiment in courses of physical or colloid chemistry.

SUMMARY

A number of simple and very inexpensive opaque rotors are now available with which measurements both of sedimentation equilibrium and of sedimentation velocity have been made with an accuracy at least as great as that obtainable with the best transparent ultracentrifuges.

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ULTRASONIC WAVES IN COLLOID CHEMISTRY¹

KARL SOLLNER²

*Department of Agronomy, New York State College of Agriculture, Cornell University,
Ithaca, New York*

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The main phenomena of interest for the colloid chemist caused by ultrasonic waves (2, 6, 13, 14, 28) are so well known that they need not be considered extensively. Ultrasonics may cause all sorts of disintegration phenomena, e.g., the formation of emulsions and of fogs, and they may bring about coagulation. Although these facts have been well known for ten years, the underlying mechanisms have been obscure; accordingly several years ago we undertook their investigation. This paper gives a short account of the work.

The experimental technique described by Wood and Loomis (28) was used. Plates about 7 cm. in diameter and 1 cm. thick, cut from quartz crystal, are placed on a lead electrode and covered with a brass ring electrode. The whole system is immersed in transformer oil, an alternating field is applied, and the quartz, which is pronouncedly piezoelectric, starts vibrating. Since the electrical frequency is the same as the mechanical frequency of the quartz plate, the vibrations are so pronounced that the oil over the quartz is set into motion and a fountain of oil rises above it. Although the quartz discs used (11) had frequencies of about 200,000 cycles a second, it must be emphasized that the frequency employed is immaterial.

If a test tube containing water and mercury or water and an immiscible organic liquid is dipped into the oil fountain, emulsification occurs at once. Gray clouds of very fine mercury droplets are thrown into the water from the water-mercury interface, and white clouds of dispersed water or organic liquid, respectively, are produced where the two liquids meet; soon more or less concentrated emulsions are obtained. These emulsions do not show any special features. In non-protected systems under our standard conditions 6 g. of mercury per liter and 50 to 60 g. of benzene or similar substances are dispersed, when the equilibrium state is reached. This occurs under our experimental conditions in approximately 1 min. In the presence of suitable emulsifiers very high concentrations can be obtained.

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² New address: Department of Physiology, University of Minnesota, Minneapolis, Minnesota.

The size of the particles (5, 7, 28) varies somewhat with the metal dispersed and the medium of dispersion; low concentration and a fluid medium of dispersion favor a higher degree of dispersion, from a few tenths of a micron to several micra, although the truly colloidal fraction in many cases is rather small.

In 1929 Richards (20) emphasized the differences in the nature of the emulsification of mercury and in the dispersion of organic liquids in water. For liquid and molten metals the mechanism of dispersion, according to him, is as follows (4, 20): When brought into the oil fountain the violent transversal vibrations of the glass tube pump small quantities of water into the liquid metal; the water droplets rising in its interior reach the interface metal-water covered with a thin film of metal. When this film breaks, a cloud of minute metal droplets is thrown into the liquid. This process, as described for the macro-interface metal-water, obviously occurs also between the water droplets in the interior of the liquid metal, thus accentuating the effect.

Figure 1 demonstrates the whole mechanism rather convincingly. A low-melting alloy was irradiated with water and cooled down during the irradiation. Its sponge-like nature is apparent from its cross section and from its surface covered with little blisters. For a reason which may be understood later, it must be stressed that this dispersion of metals occurs equally well *in vacuo* or when high external pressure is applied.

Now let us turn our attention to the mechanism of emulsification in oil-water systems³ (3), which was shown to hold quite generally, e.g., for the peptization of gels (12) or the formation of fogs (23) of organic or aqueous liquids, and for the dispersion of solids in liquids (25). The only exception is the formation of metal emulsions, discussed above.

The facts concerning emulsification in non-metallic systems, as described first by Newton Harvey (13), are as follows: Emulsification, i.e., disintegration, in general, occurs neither *in vacuo* nor when sufficiently high outside pressure is applied, the liquids in the latter case being gas-free or saturated with gas at a lower pressure only. This rule applies as well in the presence of even the best emulsifiers, where mere shaking may easily produce stable and fine-grained emulsions (3). At equilibrium pressure emulsification always occurs, provided this pressure is neither too high nor too low. The lower limit is much more sensitive in toluene-water systems, e.g., a gas pressure of at least 100 mm. of mercury is necessary.

³ L. A. Chambers and M. Newton Gaines must be given credit for prior publication of an explanation of their experiments, similar to ours, on emulsification with low frequencies. This work (J. Cellular Comp. Physiol. 1, 451 (1932)) unfortunately did not come to our attention until after the whole series of our investigations on ultrasonics had been published.

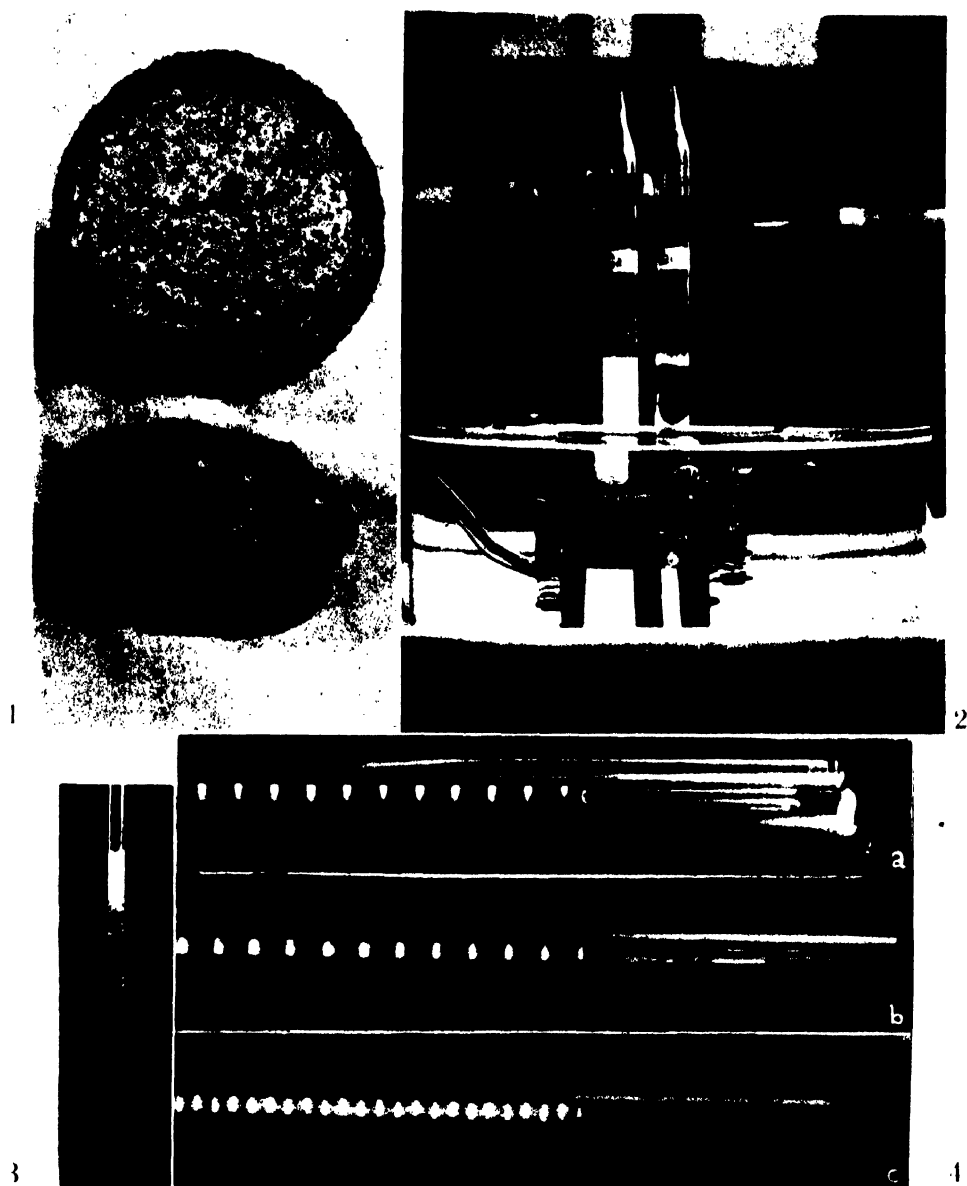


FIG. 1. Emulsification of a metal by ultrasonics. A low-melting alloy solidified during irradiation. About twice actual size.

FIG. 2. Emulsification by ultrasonics. The influence of the presence of a foreign gas upon emulsification. About one-third actual size.

FIG. 3. Coagulation of an emulsion by ultrasonics. About one-quarter actual size.

FIG. 4. Stationary wave patterns. (a) Toluene in water; (b) quartz in water; (c) toluene and quartz in water. About 1.5 times actual size.

How striking this difference is may be gathered from figure 2. The pressure experiments were performed in long test tubes. The column of the upper liquid is rather high, so that no saturation can occur in the critical region, the interface liquid-liquid, when an outside pressure is applied by means of a compressed gas.

How do the sound waves cause what at first sight appears to be such complicated phenomena, the effects being substantially the same whether performed at a few thousand or at millions of cycles a second (3)? A sound wave travelling through a liquid compresses and stretches it periodically. If the stretch is moderate and the irradiated liquid is free of gas, nothing spectacular occurs, but if the liquid is saturated with gas, gas bubbles appear, as was shown in detail by Boyle (6) and Newton Harvey (13) and their coworkers. What happens if the liquid is stretched unduly was described more than sixty years ago as a curiosity by Kundt and Lehmann (17) (working at low frequencies). They said: "While the whole system was vibrating violently the water close to the end of the vibrating rod turned turbid during the vibration. Since it was entirely free of air, these small bubbles causing the turbidity could only be due to the disruption of the water under the influence of the intense vibrations." When irradiating with ultrasonics (9, 24) in a long test tube containing a carefully degassed liquid, such as benzene, toluene, or slightly warmed water, zones of a slight and somewhat glittering opacity were always formed. Although no bubbles rose to the surface, a hissing noise was always heard.

Thus it is clearly indicated that the liquid disrupts under the stretch of sound waves, hence a high hydrostatic pressure prevents the whole phenomenon. If the same experiment is performed in a vacuum even at low energies, the liquid bubbles and boils but no hissing noise is heard. Under neither of these conditions does emulsification occur. Strong mechanical action by ultrasonics is always accompanied by the hissing noise, its loudness being so characteristic that it is used as an indicator of their efficiency. It is apparent that, although the formation of cavities does not give rise to destructive action, their disappearance, always connected with the hissing sound, does.

Lord Rayleigh (19) calculated the pressures which may occur when a vapor bubble collapses in a liquid and found that many thousands of atmospheres may be obtained locally in this way. The collapse of cavities at the rear of steamship propeller blades may cause the rapid destruction of the blades. In engineering the entire phenomenon, involving the formation of cavities and their vehement collapse due to outside pressure, is called "cavitation." This term will be used in this sense.

It may be easily demonstrated that the collapse of steam bubbles produces emulsification when occurring at the interface of two liquids. The collapse of the steam bubbles when accompanied by a rattling sound causes

rapid emulsification (3). This method of emulsification is substantially different from the older one in which the vapor of an organic liquid is introduced into water, forming an emulsion on condensation.

We may safely conclude that the emulsification by ultrasonics is due to "cavitation" as defined above (3). This accounts for the fact that no emulsification occurs in a vacuum or when a high outside pressure is applied. In a vacuum cavities may be formed, but lack of outside pressure prevents their violent collapse. On the other hand, a sufficiently high pressure prevents the formation of cavities. The prevention of cavitation by applying an outside pressure is well known in engineering.

The influence of dissolved gases will not be discussed here in detail; one of their main functions is to act as weak spots when the liquid is stretched, thus promoting cavitation (3). Similarly, cavitation is favored at the interface water-oil, a fact promoting the dispersing action.

The influence of pressure and vacuum is not observed when dispersing liquid metals since, as already mentioned, their dispersion is not due to cavitation.

The dispersion of gels (10, 11, 12), e.g., rubber in benzene, or the liquefaction of thixotropic gels, is due to the same mechanism as emulsification in oil-water systems, occurring under exactly the same conditions. This is also true for the dispersion of solid bodies in liquids (25). An efficient dispersion of this kind has not as yet been observed with metallic or other substances of great cohesion, although oxide films, etc., may be easily removed by ultrasonics. On the other hand softer substances, especially of high cleavage (such as graphite or mica), may be readily dispersed. This process proceeds at a remarkably rapid rate when semicolloidal or microscopic suspensions, but not macrocrystals, are irradiated, colloidal solutions being readily obtained (25).

It can be demonstrated also that the formation of fog (23) by ultrasonics, as described by Wood and Loomis, is due to cavitation. A beaker or test tube containing a volatile liquid, such as benzene or toluene, is rapidly filled with a white cloud or fog when irradiated. With less volatile liquids it is necessary to use high energies or, more advantageously, to concentrate the energy by means of a special collector, a test tube drawn out at the middle to a thin-walled constriction. When brought into the oil fountain the constriction vibrates violently, and even liquids of a very viscous nature and of a high boiling point are dispersed into the air, if they are allowed to run down through the constriction. Air currents set up by the rectifying action (18) of the transversally vibrating collector transport the fog droplets away from it.

The very suggestive idea that one is dealing with evaporation on account of the great heat developed at the critical spot can readily be shown to be wrong. When an oil containing a non-volatile dyestuff is used, a colored

cloud is formed around the collector, which proves that the dispersion is a direct one. Here, too, experiments at varying pressures show that cavitation causes the dispersion. On close inspection one may see how the surface becomes rippled at energies just sufficient to start fog formation. It looks as if the surface were hit from above,—indeed it is hit from above by the collapse of the cavities formed at the surface (23).

How active the interface liquid-gas is may also be seen from the following experiment: A strip of rubber partially dipped into benzene is, on irradiation, attacked most near the surface of the benzene, and may be eaten away entirely at this point, whereas its lower end, further away from the surface of the benzene, is practically free from attack.

We shall consider next the opposite of the phenomena discussed, the coagulating action of ultrasonics (21). Ultrasonics must be able to coagulate at a high speed, since a stationary state is soon reached in preparing an emulsion. It is easily demonstrated that this coagulation is not due to the streaming or stirring which is always observed during strong irradiation. Rapid coagulation occurs also at rather low energies where such a movement is never observed.

It may be shown that coagulation is due to the formation of stationary wave patterns,—Kundt's dust figures in liquids (21). When an emulsion is irradiated (the phenomenon is best seen in high columns of liquid), more whitish zones appear in the lower and middle part of the test tube, where the droplets of the emulsion accumulate. How such a test tube looks after a few minutes of irradiation may be seen from figure 3. Near the surface, where cavitation is strongest, the emulsion is not much affected, whereas in the lower parts all the dispersed material is accumulated. The process of coagulation may be observed microscopically (21). With low energies practically complete coagulation may be brought about, since the opposite process, emulsification, needs energies exceeding a rather well defined limiting value.

The coagulation of suspensions is quite analogous. In unstable systems, for instance quartz powder in organic liquids, it is very impressive. On slight irradiation the particles accumulate and stick to each other, thus forming big lumps which sink rapidly to the bottom of the tube; the whole liquid is free from particles after a few seconds.

To study the stationary wave patterns more closely, capillaries filled with an emulsion or suspension were used. They were closed at one end with picein, leaving a small air gap between the emulsion and the picein stopper, to prevent any appreciable movement of the liquid. When the oscillations are started the dispersed phase forms zones of accumulation which rapidly get very sharp; one has the impression of small disks standing upright in the capillary (figure 4). The distance between each two of the zones of

accumulation can be calculated rather exactly from the sound velocity of the liquid and the known frequency of the oscillation.

In some cases the dispersed phase is collected in the nodes; in other cases in the loops. The main decisive factor—there must be some other ones too—seems to be the ratio of the specific gravities of the dispersed phase and the medium of dispersion. If the dispersed phase is lighter, it accumulates in the nodes; if it is heavier than the medium of dispersion, in the antinodes (16). This means that in the former case the meniscus becomes free from dispersed phase; in the latter case, there is a locus of accumulation (figure 4a, 4b). When a mixed system containing, e.g., dispersed toluene and quartz powder is irradiated the two dispersed phases separate and accumulate at their proper places, in the nodes and loops, respectively (figure 4c). Larger particles are much more readily collected; particles several micra in diameter accumulate practically instantaneously, whereas smaller particles, below 0.5μ or so in diameter, are hardly affected at moderate energies and the frequency employed.

The coagulating action of the ultrasonics is now easily understood: firstly, the particles are accumulated and, as one knows, the rate of spontaneous coagulation increases rapidly as the concentration increases; secondly, particles of different size migrate with different velocities towards the zones of accumulation, thus being liable to additional collisions, a kind of orthokinetic coagulation (26, 27); thirdly, the particles do not migrate only in one direction, their macroscopic movements merely being the result of the asymmetry of the oscillations which they perform according to their (different) size; this too causes a kind of orthokinetic coagulation.

Much very interesting work has been done by other investigators (1, 15) on the coagulation of fogs and smokes. There is considerable analogy with the coagulation in liquid systems, orthokinetic coagulation being particularly pronounced with such systems (22).

In conclusion, mention should be made of the orientation of anisometric, i.e., rod- and plate-like, particles by ultrasonics (8). When a very dilute suspension of finely ground mica or graphite is irradiated even with very weak energies, brilliantly glittering zones are observed at once in transmitted or reflected light, indicating an orientation of the (anisometric) particles, perpendicular to the axis of the tube, i.e., perpendicular to the flux of energy. In this experiment the energy applied may be so weak as to cause no appreciable accumulation even over long periods.

This orientation is found with all rod- and plate-like substances of macroscopic and microscopic dimensions; it was also found with some truly colloidal systems, e.g., vanadium pentoxide sols or ferric oxide sols containing anisometric particles, ultramicroscopic in all three dimensions. The orientation with these sols is studied most conveniently with polarized light,

the orientation of the particles being in all cases perpendicular to the flux of energy; this interesting phenomenon undoubtedly needs further investigation.

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ADSORPTION AT CRYSTAL-SOLUTION INTERFACES. X

A STUDY OF THE ADSORPTION OF MONOAZO DYES BY CRYSTALS OF POTASSIUM SULFATE DURING THEIR GROWTH FROM SOLUTION¹

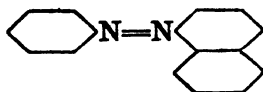
MERLE D. RIGTERINK AND WESLEY G. FRANCE

Department of Chemistry, The Ohio State University, Columbus, Ohio

Received July 14, 1938

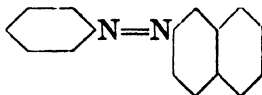
This paper is a continuation of previously reported studies made in this laboratory on the adsorption of foreign substances by growing crystals (1, 3, 5, 6, 7, 8, 10, 11, 15, 16). Attention has been focussed especially on one point which has received very little previous study,—the presence and distribution of polar groups in the foreign molecules. Only a few cases of closely related dyes where one was adsorbed and the other was not have been observed in the earlier work. Buckley (2) investigated a large number of closely related dyes but only a rather limited number which were isomeric; consequently he was unable to arrive at any general conclusions which would predict the behavior of a dye not previously investigated.

Fortunately samples of the members of two series of dyes which were admirably suited for such an investigation were obtained. These were originally prepared by Dr. Wallace R. Brode and two of his former students (4, 9) for spectroscopic investigations, and therefore are of a higher purity than the usual commercial products. These dyes were prepared by coupling aniline and the ortho-, meta-, and para-sulfonated anilines by the usual method of diazotization with a series of mono- and di-sulfonic acid derivatives of α - and β -naphthols and α - and β -naphthylamines. They will be referred to in the tables by abbreviations which are derived from the intermediates used in their preparation. These intermediates were as follows: aniline (A), ortho-sulfonated aniline (O), meta-sulfonated aniline (M), para-sulfonated aniline (P), α -naphthol (α -OH), β -naphthol (β -OH), α -naphthylamine (α -NH₂), and β -naphthylamine (β -NH₂). The numbers given in the tables after the abbreviations refer to the positions of the —SO₃Na groups attached to the naphthalene rings. The dyes which are starred in the tables possess the nucleus



¹ Presented at the Fifteenth Colloid Symposium, held at Cambridge, Massachusetts, June 9-11, 1938.

while the others possess the nucleus



EXPERIMENTAL

Potassium sulfate was selected for this investigation, since preliminary experiments showed that it adsorbed a number of the dyes of these series. Qualitative experiments were made to determine which of the dyes were adsorbed, and therefore which should be chosen for further quantitative experiments. In 50 cc. of a saturated potassium sulfate solution was dissolved 0.005 ± 0.0005 g. of each dye. These solutions were then set aside in 50-cc. beakers, and slow evaporation allowed to take place at room temperature. The resultant crystals were examined for adsorption and habit modification.

For the quantitative experiments equal molar concentrations of dye rather than equal weight concentrations were used. A concentration of 2×10^{-5} moles of dye per 100 cc. of solution was chosen for this purpose, since for the majority of the dyes this is approximately equal to the 0.01 per cent concentration by weight used in all of the qualitative experiments. 1×10^{-4} mole of each dye was dissolved in 500 cc. of a saturated potassium sulfate solution. The resulting solution was filtered and set away in eight 100-cc. beakers to crystallize by slow evaporation at $30^\circ\text{C.} \pm 0.1^\circ$ at constant humidity for 96 hr.

In those cases in which the dyes were slightly soluble the solutions were prepared by dissolving the dye in a hot saturated potassium sulfate solution and then allowing the mixture to stand at 30°C. for two days to allow the excess dye to precipitate out.

The crystals were removed after their growth, rinsed twice with distilled water, dried above an electric oven at a temperature of $50\text{--}60^\circ\text{C.}$, and allowed to cool in a desiccator containing Drierite (anhydrous calcium sulfate). A portion of the crystals was then weighed, dissolved in water, and diluted to 100 cc. A standard solution with an approximately equal dye concentration was also prepared. The two solutions were then compared in a Lcitz colorimeter with an average of ten readings taken as the colorimeter reading used in the calculation. From these data the number of moles of dye adsorbed, per mole of potassium sulfate that crystallized, was calculated.

RESULTS

The results obtained are summarized in tables 1, 2, 3, and 4. In the second determinations appearing in the tables a new crop of crystals was

used for the analysis, and an equal concentration of the salt was used in the standard solutions.

In table 5 are given the results of quantitative measurements made of the amount of adsorption of P- β -OH-6 at a number of different concentrations. The results above concentrations of 3×10^{-5} moles of dye per 100 cc. of solution are not quite as accurate as the results at lower concen-

TABLE 1
Summary of effect of soluble acid dyes on potassium sulfate

DYE	PER CENT PURITY	MOLES OF DYE ADSORBED (PER MOLE OF K ₂ SO ₄) $\times 10^4$			MODIFICATION
		First determination	Second determination	Average	
P- β -OH*	84.63	91	103	97	Types 1 and 2
M- β -OH-6*	71.25	87	94	90.5	Type 1
M- β -OH-7*	74.15	79	97	88	Type 1
P- β -OH-6*	66.40	49	50	49.5	Type 2
P- β -OH-6:8*		24	22	23	Type 1
O- β -OH-7*	98.87	14	13	13.5	Type 3
O- β -OH-6*	93.05	8.9	9.1	9.0	Type 3
P- β -OH-7*	61.25	4.3	4.0	4.25	Type 1
M- α -OH-3	54.61	3.7	3.5	3.6	Types 4 and 5
M- α -OH-4	77.87	1.9	1.7	1.8	Type 5
O- β -OH-3:6*	46.01	0.8	0.7	0.75	None
M- α -OH-3:8	68.28	<1.0			Type 5
O- α -OH-5	82.39	<1.0			None
O- α -OH-3:8	55.10	<1.0			Type 5
A- α -OH-3	90.25	0			None
A- β -OH-6*	62.75	0			None
A- β -OH-6:8*	89.99	0			None
P- α -OH-3	62.52	0			None
P- α -OH-4	62.20	0			None
P- α -OH-5	63.00	0			None
P- α -OH-3:8	96.66	0			None
M- α -OH-5	73.99	0			None
M- β -OH-6:8*	43.41	0			None
O- α -OH-4	93.86	0			None

tration, owing to the fact that it was difficult to induce crystallization at the higher concentrations of dye.

The types of crystals referred to in the tables are as follows: *Type 1*. These consisted of very thin plates growing in several directions from a central axis. Often there were several of these very thin sheets growing close together and parallel to one another from the central axis, and then there would not be any more for an angle of about 45-60°, when another set of parallel sheets grew outward. The coloration in these crystals was

very high and quite uniform throughout. This coloration, however, was produced by adsorption on the (111) and (110) faces only, as shown by a further experiment with the dye M- β -OH-7. When crystals of potassium sulfate were grown from solutions containing only one-fourth the concentration of dye used in the previous experiments, the dye could be seen strongly adsorbed on the above two faces, while the other faces were almost free of color. This adsorption produced small grooves down the edges of the crystals, but aside from this there was no modification of the habit.

Type 2. These also were quite highly and uniformly colored but grew in the form of needles, varying considerably in diameter and often growing in bunches with the needles running parallel to one another or sometimes individually forming a network on the bottom of the beaker. The adsorp-

TABLE 2

Summary of effect of acid dyes forming a saturated solution with potassium sulfate solution

DYE	PER CENT PURITY	SOLUBILITY	MOLES OF DYE ADSORBED (PER MOLE OF K ₂ SO ₄) $\times 10^4$	MODIFICATION
M- α -OH*	83.75	Slightly soluble	25	Types 3 and 4
P- α -OH*	70.00	Nearly soluble	16	Types 3 and 4
M- β -OH-3:6*	69.57	Slightly soluble	8.1	Type 3
A- α -OH-5	53.13	Nearly soluble	7.9	Type 2
M- β -OH*	88.00	Slightly soluble	2.6	Type 5
A- α -OH-4	79.25	Slightly soluble	1.6	None
O- α -OH-3	63.98	Nearly soluble	<1.0	None
A- α -OH-3:8	58.16	Slightly soluble	0	None
A- β -OH*		Insoluble	0	None
A- β -OH-7*	83.00	Slightly soluble	0	None
O- α -OH*	62.75	Slightly soluble	0	None
O- β -OH*	49.00	Insoluble	0	None

tion in this case occurred mainly on the (110) plane, as shown by crystals of potassium sulfate grown in half the previous concentration of P- β -OH-6. There was also a very small amount of adsorption on the (010) planes. With these crystals the growth perpendicular to the (110) face was apparently decreased enough to make these faces the prominent ones, and thus the long diamond-shaped needles were produced.

Type 3. These were examples in which there was very pronounced twinning. Practically all of these twins were of the triplet variety, in which there was an incomplete interpenetration of the individuals. The deepest coloration seemed to be in the angles of these "three-rayed stars." The production of these twins is not readily explained, although it is presumably connected with the deposition of the dye. Twins in pure potassium sulfate

TABLE 3

Summary of effect of soluble basic dyes on potassium sulfate

DYE	PER CENT PURITY	MOLES OF DYE ADSORBED (PER MOLE OF K_2SO_4) $\times 10^3$			MODIFICATION
		First determination	Second determination	Average	
M- α -NH ₂ -6*	94.50	83	83	83	Type 1
A- β -NH ₂ -7*	76.13	31	32	31.5	Type 2
P- α -NH ₂ -7*	94.10	24	22	23	Type 1
P- α -NH ₂ -2*	87.26	6.0	7.1	6.6	Very long needles; uneven adsorption
M- α -NH ₂ -2*	89.97	5.7	5.7	5.7	Type 4
O- α -NH ₂ -2*	97.28	3.5	4.1	3.8	Type 4
M- α -NH ₂ -8*	87.47	3.2	3.0	3.1	Type 4
M- β -NH ₂ -7*	71.80	2.8	2.4	2.6	Type 5
M- α -NH ₂ -7*	89.76	1.8	2.3	2.05	Type 4
M- α -NH ₂ -4	89.76	1.8	1.7	1.75	Type 5
A- α -NH ₂ -3	75.40	<1.0			None
A- α -NH ₂ -4	83.55	<1.0			None
P- β -NH ₂ -5*	61.40	<1.0			None
P- β -NH ₂ -6*	87.27	<1.0			None
P- β -NH ₂ -7*	83.56	<1.0			None
M- α -NH ₂ -3	88.64	<1.0			None
M- α -NH ₂ -5	91.66	<1.0			None
O- α -NH ₂ -6*	83.16	<1.0			None

DYE	PER CENT PURITY	MOLES OF DYE ADSORBED $\times 10^3$	MODIFICATION
P- α -NH ₂ -3	71.28		None
P- α -NH ₂ -4	80.00		None
P- α -NH ₂ -5	91.55		None
M- β -NH ₂ -5*	90.58		None
M- β -NH ₂ -6*	90.99		None
O- α -NH ₂ *	93.12		None
O- α -NH ₂ -3	76.48		None
O- α -NH ₂ -4	87.37		None
O- α -NH ₂ -5	79.00		None
O- α -NH ₂ -7*	65.96		None
O- α -NH ₂ -8*	82.14		None
O- β -NH ₂ -5*	92.25		None
O- β -NH ₂ -6*	96.87	0	None
O- β -NH ₂ -7*	69.00	0	None

occur rather frequently on the (110) plane, although in such cases there is usually a complete interpenetration of the individuals.

Type 4. These were almost rectangular crystals, in which the dye was only adsorbed on the (110) planes, producing an hour-glass effect with

parts of the crystal colorless and other parts of it colored. In this case the chief modification occurred on the (010) faces, making them the most prominent ones even though the adsorption occurred only on the (110) planes.

TABLE 4

Summary of effect of basic dyes forming a saturated solution with potassium sulfate solution

DYE	PER CENT PURITY	SOLUBILITY	MOLES OF DYE ADSORBED (PER MOLE OF K_2SO_4) $\times 10^6$	MODIFICATION
A- β -NH ₂ -6*	85.49	Slightly soluble	33	Type 2
P- β -NH ₂ *	88.83	Slightly soluble	22	Type 1
A- β -NH ₂ -5*	92.47	Slightly soluble	20	Type 1
P- α -NH ₂ *	84.59	Slightly soluble	15	Type 4
P- α -NH ₂ -8*		Nearly soluble	11	Type 1
M- β -NH ₂	93.23	Nearly soluble	7.8	Types 1 and 2
P- α -NH ₂ -6*	90.78	Nearly soluble	7.4	None
A- α -NH ₂ -5	66.92	Nearly soluble	3.1	Type 5
M- α -NH ₂ *	96.34	Slightly soluble	1.4	None
A- α -NH ₂ *		Insoluble	0	None
A- α -NH ₂ -2*	87.16	Slightly soluble	0	None
A- α -NH ₂ -6	66.39	Nearly soluble	0	None
A- α -NH ₂ -7	92.88	Slightly soluble	0	None
A- α -NH ₂ -8	92.96	Slightly soluble	0	None
A- β -NH ₂ *		Insoluble	0	None
O- β -NH ₂ *	80.90	Slightly soluble	0	None

TABLE 5

Summary of adsorption of P- β -OH-6 by potassium sulfate from solutions of various concentrations

CONCENTRATION OF DYE MOLES PER 100 CC. $\times 10^6$	MOLES OF DYE ADSORBED (PER MOLE OF K_2SO_4) $\times 10^6$
1	9
2	50
3	108
4	167
5	171
6	174
8	257
10	232
12	273

Type 5. These were crystals that had little if any modification of habit, A striking feature was that they were approximately five to ten times larger than the crystals of potassium sulfate obtained from pure solutions under the same conditions. The small amount of adsorption did not seem to

be concentrated upon any one face, but there was a slight uniform tinge of color throughout.

As an aid in interpreting the data and to account for the fact that the adsorption generally occurred on the (110) and the (111) planes, scale models of both dye molecules (figure 1) and the potassium sulfate crystal were constructed (figure 2). The dimensions of the unit cell as determined by Ogg and Hopwood (13, 14) were used for this purpose. The hydrogen atoms in the dye molecule were assigned the dimensions of the atomic domain of hydrogen as calculated by Mack (12).

The potassium sulfate model (figure 2) clearly showed the (100) planes to be populated by mixtures of K^+ and SO_4^{--} ions, and the (110) and (111) planes to be predominantly K^+ or SO_4^{--} ions. The ionic grouping in the (110) and (111) planes should therefore result in these planes having

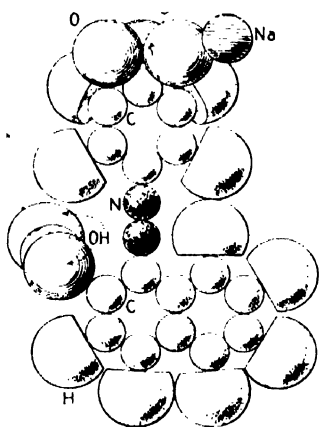


FIG. 1

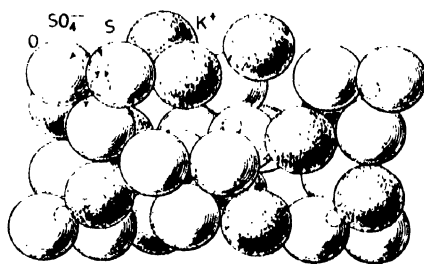


FIG. 2

FIG. 1. Model of dye P- β -OH

FIG. 2. Model of potassium sulfate. Side elevation (100) plane

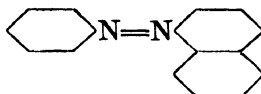
strong adsorptive forces, and in the absence of interfering factors, such as steric hindrance, one would expect the adsorption to occur on the (111) and (110) planes in preference to the (100) plane. The collected data are in most instances in accord with this prediction.

The mode of attachment of the dye molecule is probably through the oxygen triangle possessed by the $-SO_3Na$ group of the dye, as previously suggested by Buckley (2). The dyes ionize in solution giving a sodium ion and a large anion possessing a number of charges equal to the number of substituent $-SO_3Na$ groups. The dye anion, therefore, has three oxygen atoms in an equilateral triangle attached to a sulfur atom exactly as in an SO_4^{--} ion, with the rest of the large dye molecule attached in place of the fourth oxygen. The $-SO_3$ group of the anion could, therefore, be drawn into the place ordinarily occupied by the SO_4^{--} ion, with

the remainder of the large dye molecule left to obstruct further crystal growth.

A study of the tables brings out a number of interesting facts. For example, the presence of a benzene ring with no substituent groups appears to be detrimental. Also the presence of the $-\text{SO}_3\text{Na}$ group adjacent to the $-\text{N}=\text{N}-$ group renders the dye less effective. This may be explained on the basis of steric hindrance. By means of the molecular dye models it was clearly evident that whenever the $-\text{SO}_3\text{Na}$ group is adjacent to the $-\text{N}=\text{N}-$ group it is so protected by nearby hydrogen atoms that it cannot present the oxygen triangle to any given plane of the crystal even though the dye molecules are not linear. There are also some structural hindrances when the $-\text{SO}_3\text{Na}$ group is in the 1-, 4-, 5-, or 8-position in the naphthalene ring. Dyes containing the $-\text{SO}_3\text{Na}$ groups at these positions, therefore, would likewise not be very effective. This leaves only the meta and para positions in the benzene rings and the 6- and 7-positions in the naphthalene rings. The data in the tables bear out the conclusion that these would normally be the most effective positions for the $-\text{SO}_3\text{Na}$ groups.

A combined study of the tables of data and the formulas of the dyes reveals the fact that in general the dyes produced from the β -naphthol-sulfonic acids are much more effective than those produced from the α -naphtholsulfonic acids. If $-\text{NH}_2$ groups are substituted for the $-\text{OH}$ groups, however, the situation is exactly reversed. In this case the dyes formed from the α -naphthylaminesulfonic acids are much more effective than those formed from the β -naphthylaminesulfonic acids. This suggests that the dipole moment of the foreign molecule must be considered in the adsorption process. Thus, if attention for the moment is confined to the dyes which are starred in the tables (those possessing the



basic structure), the above facts simply mean that the most effective position for the $-\text{OH}$ group is ortho to the $-\text{N}=\text{N}-$ group, while the most effective position for the $-\text{NH}_2$ group is the para or 4-position in the naphthalene ring. Williams (17) gives -1.5 Debye units as the dipole moment of the $-\text{OH}$ group and $+1.7$ Debye units for the dipole moment of the $-\text{NH}_2$ group. Therefore, assuming that the other groups remain in the same positions, the dipole moments of the dye molecules would be more nearly the same if the $-\text{OH}$ group were ortho and the $-\text{NH}_2$ group para to the $-\text{N}=\text{N}-$ group. This then suggests a plausible reason for the differences pointed out above.

The results of the quantitative measurements of the amount of adsorption of P- β -OH-6 at a number of concentrations is graphically shown in

figure 3. The results are obviously in complete agreement with previous work (1, 3, 5, 6, 7, 8, 10, 11, 15, 16), in that there is a minimum concentration below which no adsorption takes place and above which the adsorption gives a typical adsorption curve. The adsorption can, therefore, be represented by the expression developed earlier (3):

$$a = kc^{1/n} - k'c^{-1/n'}$$

In other qualitative experiments it was shown that none of the dyes was adsorbed by potassium alum and none of the acid dyes by ammonium alum. The basic dyes were not investigated with the latter salt. Hydrochloric acid was found to increase the amount of adsorption of the dye P- β -OH-6 by potassium sulfate, and sodium hydroxide decreased the amount.

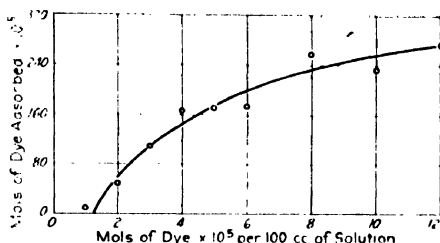


FIG. 3. Adsorption of P- β -OH-6

SUMMARY

1. The results obtained in this investigation have been found to be in harmony with the theory that adsorption by a growing crystal is dependent on (1) the residual valency force fields of the crystal faces, (2) the interionic distances within the faces, (3) the concentration of the foreign substance in the solution, and (4) the presence and distribution of polar groups in the foreign molecules. However, it may be only necessary for one of the substituent groups to fit into the ionic planes of the faces.

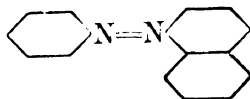
2. Adsorption of foreign substances is highly specific, with only a few crystalline substances adsorbing a given series of dyes.

3. Adsorption of foreign substances usually produces a habit modification, although the modification may be on faces other than those upon which the dye is adsorbed.

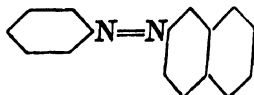
4. Twinning in crystals can be made very much more pronounced by the adsorption of some foreign substances. This suggests the possibility that twinning in general may be caused by the adsorption of a very minute amount of impurity at some favorable point during the growth of the crystal.

5. The mode of attachment of these monoazo dyes to crystals of potassium sulfate may be through the oxygen triangle of the $-\text{SO}_3\text{Na}$ groups.

6. Dyes with the



basic formula are much more strongly adsorbed than those possessing the



basic formula.

7. An "empty" benzene ring is detrimental to adsorption, as is a $-\text{SO}_3\text{Na}$ group adjacent to the $-\text{N}=\text{N}-$ group. The most active positions for the $-\text{SO}_3\text{Na}$ groups are meta and para to the $-\text{N}=\text{N}-$ group in the benzene ring and in the 6- and 7- positions in the naphthalene ring.

8. The change of an $-\text{OH}$ group to an $-\text{NH}_2$ group has a profound effect on the adsorption in a manner which indicates that the dipole moment of the molecule is concerned.

9. The adsorption of the dye P- β -OH-6 followed the expression:

$$a = kc^{1/n} - k'c^{-1/n'}$$

The authors wish to take this opportunity to acknowledge their indebtedness to Dr. Wallace R. Brode and his former students, Dr. Marion E. Griffith and Dr. Dale R. Eberhart. All of the dyes used in this investigation were prepared by them, and they very generously supplied the samples which made this investigation possible. The purities of the dye given in the tables were also determined by them.

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EXPANSION PATTERNS OF PROTEIN MONOLAYERS ON WATER¹

VINCENT J. SCHAEFER

Research Laboratory, General Electric Company, Schenectady, New York

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When a monolayer of a protein is formed on a water surface, it exists as a homogeneous, insoluble, reversibly compressible (8, 6), two-dimensional structure with certain properties characteristic of the specific proteins.

Protein monolayers can be formed by a number of methods: for example, from a small amount of dried protein placed on the water surface (5), from a small amount of dissolved protein ejected from a micropipet inserted parallel and half submerged in the water surface (4), from drops of a solution placed on a flat plate dipped into the water, by dissolving the protein in the bulk substrate followed by subsequent stirring, or by spreading the protein on a strong salt solution followed by removal to another tray (7). As has been shown by many investigators, a protein spreads best at or near its isoelectric point.

Protein monolayers spread and deposited under low pressures show thicknesses ranging from 6 Å. to 18 Å., depending on the specific protein used. This paper will describe a very simple technique for rendering such films visible and will indicate the possibilities available for following changes in molecular structure, orientation, and other characteristics which are related to the fundamental properties of the native protein.

The apparatus required for studying expansion patterns is exceedingly simple. A shallow tray with flat edges, several barriers for cleaning the water surface, suitable illumination, and a few drops of indicator oil comprise the total necessary equipment.

Our trays are made of $\frac{1}{8}$ -in. angle brass fastened to a $\frac{1}{8}$ -in. flat sheet of the same material, the joints being water-proofed and the inside covered with black Bakelite paint. A mixture of carbon black and paraffin applied hot will serve satisfactorily. The black background which emphasizes the contrasting intensities may also be obtained by using a sheet of cobalt glass or Bakelite in the bottom of the tray or by coating the outside of a glass tray with black paint.

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Dr. K. B. Blodgett has previously described the preparation of indicator oil (2). Automobile oil oxidized by prolonged heating is mixed with pure mineral oil. When placed on clean water this mixture spreads to form thin films of a definite thickness, depending on the amount of the oxidized material added. For observing expansion patterns a mixture which produces a thickness of about 1500 Å. and a first-order yellow film when viewed at 45° has proved to be very satisfactory.

Several lamps placed behind a sheet of opal glass (milk glass) provide a very fine source of diffuse illumination for viewing the patterns. Daylight interspersed by a sheet of translucent paper also works quite well.

FORMATION OF AN EXPANSION PATTERN

In order to illustrate what is meant by the expansion pattern of a protein, let us use a sample of pepsin. The important steps are illustrated in figure 1. Distilled water at equilibrium with the air at pH 5.8 is placed in the tray. The surface is cleaned by sweeping several times with barriers, and enough indicator oil is applied to cover three-quarters of the clean surface. A cleaned platinum wire transfers a small amount of pepsin in the form of powder to the center of the surface area. It spreads on the water, forming an invisible film whose advancing border will be seen as it drives the indicator oil ahead of it in radial directions. In the case of pepsin, this advancing film will be seen to present a smooth rounded concentric edge, of a radius equal to the distance from the point of application. The outline of the advancing boundary of the monolayer is often characteristic of specific proteins and will be referred to from time to time. Care should be observed that only enough protein is applied so that the remaining free surface is nearly covered with a monolayer.

After the monolayer is spread, barriers are used to push the surrounding indicator oil into intimate contact with the outer edge of the monolayer, care being taken that the monolayer is not subjected to any degree of pressure. This is controlled by stopping compression before any change in color of the indicator oil occurs. A perceptible change in color equals a pressure of $F' = 1$ dyne per centimeter. After intimate contact is reached with the oil and the monolayer, a small drop of indicator oil is placed in the central portion, and will in the case of pepsin expand to produce a geometrical figure of a star-like form, with the indicator oil showing a peculiar gradation in color intensity, appearing thinner than normal at the monolayer boundary. If other portions of the monolayer are treated in a similar way, patterns identical in every respect will be observed, indicating that the film possesses a structure which is uniform throughout, showing no memory of the point of formation.

Because of their high compressibility, many proteins, if permitted, will spread on the water to build up pressures of more than 10 dynes per centimeter. Most proteins exhibit varied changes in expansion pattern as the

surface pressure is increased. Egg albumin, for example, when subjected to a compression of 35 dynes in one direction will show a fibrous structure when expanded by a high-pressure indicator oil, while still under pressure, with the fibrous sheets oriented parallel to each other at right angles to the direction of compression. Such sheets may be lifted from the water surface as threads and when dried are nearly invisible.

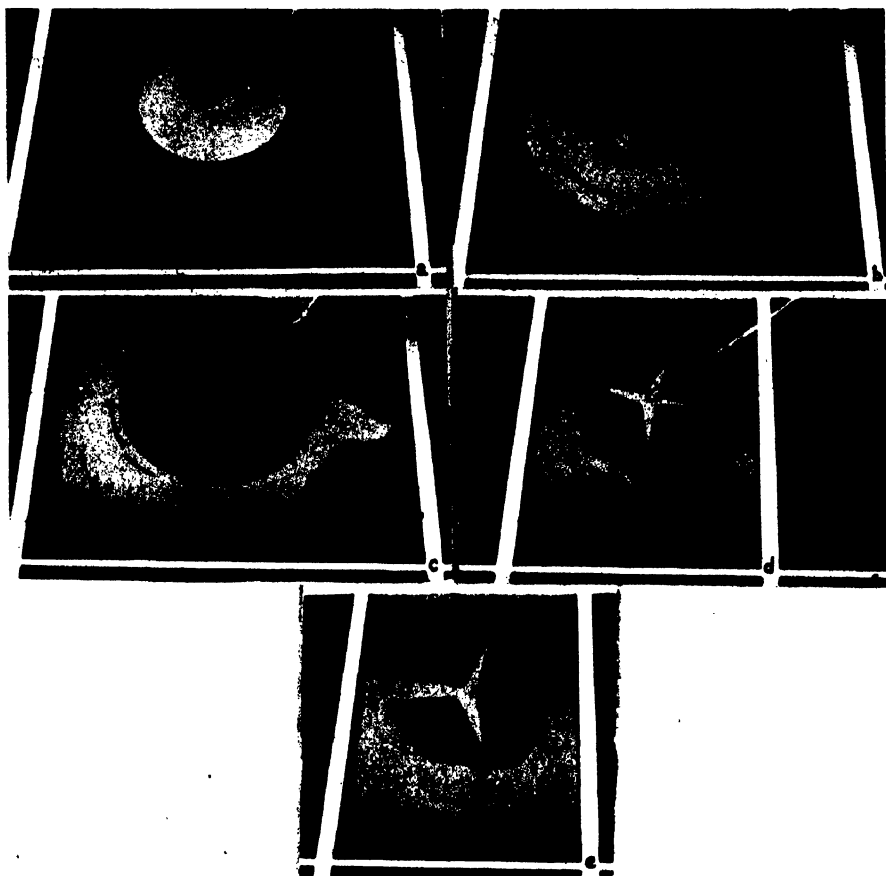


FIG. 1. Formation of expansion patterns. a, applying indicator oil; b, indicator oil spreading; c, applying protein monolayer; d, expanding monolayer; e, pepsin expansion pattern.

CLASSIFICATION OF EXPANSION PATTERNS¹

Expansion patterns of the proteins studied may be roughly divided into three general groupings of geometrical configuration. The terms "star-like," "rough circular," and "smooth circular" will serve to describe these three classes.

"Star-like" refers to patterns which expand at low pressure to produce

figures related in configuration to a star. Although five-pointed stars are often formed, the number of points observed varies from three to six. Typical examples of these figures may be found with pepsinogen, tobacco seed globulin, and trypsinogen, illustrated in figure 2. In certain cases, particularly with pepsin and trypsinogen, the star form produced by the expansion of the indicator oil is further modified by a peculiar gradation in the color of the indicator oil, producing a thinning out of the oil film which under normal conditions is exceptionally uniform. The protein monolayers which produce expansion patterns of the star-like form are, in general, of the type described by Hughes and Rideal as a gel structure. It should be noted here, however, that the gel-like monolayers considered in this paper are formed spontaneously at very low pressures of the order of 0.5 to 1.0 dyne per centimeter and in general are found to be characteristic of the specific protein, regardless of the spreading method used. That higher pressure often produces a film of the gel type from a liquid monolayer may be observed if gliadin acetate is compressed to 15 dynes per centimeter. Under this compression this protein, which is very liquid under low pressure, shows a typical star-like expansion pattern.

While about half of the proteins studied show the general star-like expansion pattern, each one has its own modification of the general form. Aside from the question of pH and relation to the isoelectric point, there are other characteristics peculiar to the specific protein. Thus the advancing edge of the monolayer in the case of pepsin is smoothly circular, while with egg albumin it is very irregular, with the indicator oil forming peculiar wedge-like structures which divert the advancing edge of the monolayer to either side to produce the irregularity mentioned.

In the rough circular classification trypsin, papain, and wheat gliadin may be used as examples (figure 3). This form is characterized by an expansion pattern whose general form is circular, but when examined locally the edge exhibits a roughened appearance, the extent of irregularity being characteristic of the specific protein used. Thus trypsin produces a circular advancing edge but an internal slightly ragged outline, with the peculiar grading in indicator oil color observed with pepsin and trypsinogen. With wheat gliadin, on the other hand, both external and internal patterns are identical, the outline being very jagged.

The smooth circular form is characteristic of such proteins as zein, gelatin, and protamine (figure 4), and of films formed by proteins in an advanced stage of denaturation or by protein degradation products which still form monolayers.

EFFECT OF DENATURATION ON EXPANSION PATTERNS

Many investigators (1, 3, 9, 10) have shown that protein solutions, when subjected to treatment such as heating, ultraviolet radiation, and



FIG. 2. Star-like expansion. a, pepsinogen; b, tobacco seed globulin; c, trypsinogen



FIG. 3. Rough circular expansion. a, trypsin; b, papain; c, wheat gliadin



FIG. 4. Smooth circular expansion. a, gelatin; b, zein; c, protamine



FIG. 5. Effect of heat denaturation of pepsin. a, 2 min. at 65°C.; b, 5 min. at 65°C.; c, 7 min. at 65°C.; d, 25 min. at 65°C.

shaking, tend to alter the protein in such a way as to modify its native properties. In the case of pepsin this modification generally parallels loss in activity of its enzymatic properties. When 0.1 per cent solutions of pepsin are subjected to such denaturation processes, the loss of activity is strikingly demonstrated by the change in expansion pattern. In the case of pepsin the star-like pattern gives way to a circular form, the pattern showing a rapid transition, the first changes appearing before the loss of activity becomes readily detectable by the change in the power of pepsin to clot milk (6).

When a 0.1 per cent solution of pepsin (Lilly), held in a quartz tube 15 cm. from an ultraviolet lamp of 1.2 amperes and 145 volts, emitting wavelengths of 2536 Å. and up, was irradiated for 5 min., no change in activity or expansion pattern was found. When irradiated for 10 min., the pattern was completely changed, while the protein had lost but 4 per cent of its original activity. The pattern had become entirely circular after 15 min. with 25 per cent loss in activity, although the area which a given amount of protein covered remained about the same. After 30 min. of irradiation, the activity showed a 68 per cent loss, and now the actual area covered had decreased to less than half of that covered by the same amount of solution irradiated for 15 min.

The alteration in expansion pattern when a solution of pepsin is subjected to a vigorous shaking will now be considered. One hundred cubic centimeters of a 0.1 per cent pepsin solution in a half-liter bottle was placed in a machine which produces 400 movements a minute, the distance of travel for each stroke being 5 cm. Samples of the solution were withdrawn at definite time intervals, and the same amount of solution used for producing a monolayer on water.

The transition in expansion pattern showed a considerable change after only 1 min. of shaking, the alteration in pattern again shifting from the star-like to the circular form, as with the deactivation by ultraviolet irradiation. The ability of the pepsin to clot milk after 1 min. of shaking had decreased by more than 60 per cent. After 5 min. of shaking, the area of film produced showed about a 50 per cent decrease with the activity decreased by 83 per cent. After 10 min. of shaking the area of film had decreased still more, with the activity decreased by 88 per cent with no further change in expansion pattern.

When a solution of pepsin at pH 5.8 is subjected to an elevated temperature, it rapidly loses its enzymatic properties, which again is indicated by the change in pattern. A 0.1 per cent solution of pepsin was heated at 65°C. for definite periods of time; then it was chilled to room temperature and the expansion patterns observed. Heating for 2 min. failed to produce any apparent change in pattern, and activity measurements showed the pepsin retained its full power to clot milk. When heated for 3 min.,

however, the pattern indicated a slight change, and the milk-clotting test showed a 16 per cent decrease in activity. After 5 min. the activity had decreased 28 per cent, and the pattern changed to a very broad star form. After 10 min. the pattern was an irregular figure approaching a circle with

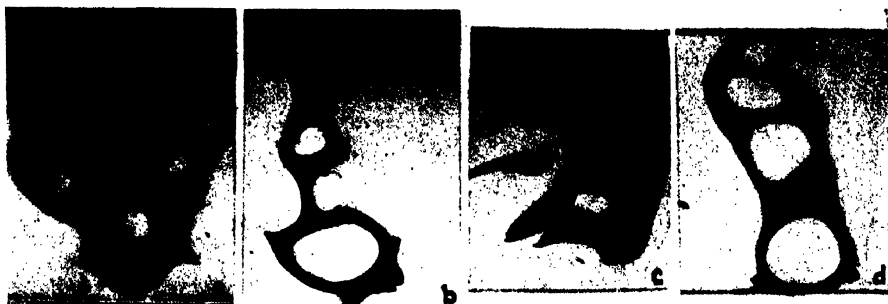


FIG. 6. Pepsin denaturation. a, irradiated with ultraviolet light for 10 min.; b, irradiated with ultraviolet light for 30 min.; c, shaken for 1 min.; d, shaken for 10 min.

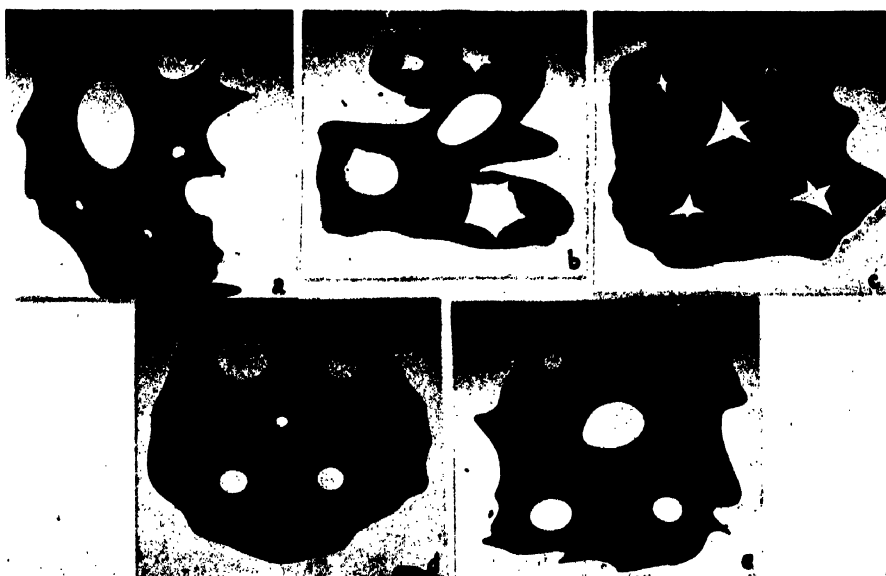


FIG. 7. Effect of dissolved salts on expansion patterns. a, insulin; b, insulin + 10^{-4} M zinc chloride; c, insulin + 10^{-4} M cupric chloride; d, gliadin acetate; e, gliadin acetate + 10^{-4} M cupric chloride.

a decrease in activity of 38 per cent; after 25 min. the pattern was a perfectly smooth circle, and the pepsin then showed a loss in activity of 62 per cent. The alterations in pattern and area due to the various types of denaturation are shown in figures 5 and 6.

Gorter (3) has shown that the addition of a very small amount of pepsin to solutions of proteins greatly increases their tendency to form monolayers. When a solution of egg albumin containing 10 mg. of the protein, partly coagulated by heating, was inoculated with 0.01 mg. of pepsin and the pH of the solution held at 4.6, the monolayer formed from a given amount of protein covered seven times the area of the control. The expansion pattern was of the smooth circular type, and gradually reverted to the star-like form as the film remained on the water. When the same procedure was followed with the pH of the inoculated solution held at 2.0,

TABLE 1
General classification of expansion patterns

PROTEIN	PATTERN FORM AT $F = 0.5$ TO 1.0 DYNE PER CENTIMETER		
	Star-like	Rough circular	Smooth circular
Egg albumin.....	x		
Pepsin.....	x		
Pepsinogen.....	x		
Trypsin.....		x	
Trypsinogen.....	x		
Urease.....	x		
Edestin.....	x		
Tobacco seed globulin.....	x		
Tobacco mosaic virus*.....	x		
Wheat gliadin.....		x	
Gliadin acetate.....			x
Zein.....			x
Papain.....		x	
Casein.....			x
Protamine.....			x
Insulin.....			x
Protamine-insulin.....			x
Gelatin.....			x

* Formed on saturated ammonium sulfate solution.

the area covered twice that of the control, showing a smooth circular expansion pattern which remained unchanged with time.

EFFECT OF DISSOLVED SALTS ON EXPANSION PATTERNS

The expansion pattern of pure insulin when spread on distilled water at pH 5.8 was found to be circular in form. When a 10^{-4} molar solution of cupric chloride was added to the water, the expansion pattern of insulin spread in the same manner showed a major change, exhibiting the star-like pattern somewhat similar to pepsin. With the same concentration of zinc

chloride a different form was found, showing much less molecular cohesion than was exhibited by insulin spread on water containing cupric ion.

In order to determine whether cupric ion might cause the same alteration in pattern with other proteins, gliadin acetate was spread on the cupric chloride solution which produced the striking change in the insulin pattern. No alteration in the normal circular pattern of gliadin acetate could be found. It would thus appear that the insulin molecule has reactive groups which readily combine in a specific manner with certain divalent ions to produce a definite change in the monolayer. These effects are shown in figure 7.

TABLE 2
Expansion patterns of proteins

PROTEIN	PATTERN FORM AT $P = 0.5$ TO 1.0 DYNE PER CENTIMETER		
	Star-like	Rough circular	Smooth circular
Pepsin.....	x		
Pepsin denatured by ultraviolet irradiation			x
Pepsin denatured by heat.....			x
Pepsin denatured by shaking.....			x
Insulin.....			x
Insulin + 10^{-4} M copper chloride.....	x		
Insulin + 10^{-4} M zinc chloride.....	x		
Gliadin acetate.....			x
Gliadin acetate + 10^{-4} M copper chloride.....			x
Wheat gliadin.....		x	
Wheat gliadin + 0.01 N acetic acid.....			x
Wheat gliadin + 0.01 N hydrochloric acid.....			x
Wheat gliadin + 0.01 N ammonium hydroxide.....		x	
Egg albumin.....	x		
Egg albumin + 0.01 N hydrochloric acid.....	x		
Egg albumin + 0.01 N ammonium hydroxide.....	x		

EFFECT OF pH ON EXPANSION PATTERN

Wheat gliadin spread in dry form on distilled water at pH 5.8 exhibited an expansion pattern of jagged outline, both internally and externally, and was very different from gliadin acetate, which produced a circular pattern in both respects. When the gliadin was spread on 0.01 N acetic acid (pH 3.4), the pattern was identical with that of the gliadin acetate. Since 0.01 N hydrochloric acid (pH 2.0) also produces a circular pattern, it is quite probable that the pH is a factor in producing the change in

pattern. It should be noted, however, that a change in pH does not have the same result with a protein such as egg albumin, which retains its star-like pattern at pH 5.8, 3.4, 2.0, and 10.6 with only slight modifications. When the gliadin was spread on 0.01 *N* ammonium hydroxide (pH 10.6), it had a pattern nearly the same as that found at pH 5.8. Wheat gliadin dissolved in 70 per cent ethyl alcohol produced a monolayer identical with that of gliadin acetate in its pattern.

Table 1 is a general classification of observed expansion patterns of proteins spread on the cleaned surface of distilled water at pH 5.8. While it is realized that proteins spread best at or near their isoelectric points, it is significant that no change in the observed patterns could be found when special buffered solutions were used at the isoelectric points of specific proteins. The only difference was the greater area of monolayer formed for a given amount of protein when spread at the isoelectric point. This observation is due probably to the fact that the pH 5.8 is not very far from the isoelectric point of most of the proteins used.

Table 2 records a number of alterations in the expansion patterns of specific proteins by changes in the composition of the substrate solution or by alterations in the protein before spreading.

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THE SOLUTION OF INSOLUBLE DYES IN AQUEOUS DETERGENTS¹

JAMES W. McBAIN AND TS-MING WOO²

Department of Chemistry, Stanford University, California

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Our investigations have previously established that many colloidal solutions form spontaneously from their constituents, and that they are thermodynamically stable (9), like ordinary solutions, entering into true reversible equilibria both within the solution and in respect to other phases in contact with them.

We showed that, in the presence of stable colloid, other unstable or insoluble substances could likewise dissolve to form thermodynamically stable colloidal systems, comprising true reversible equilibria, the properties of the solutions being independent of previous history and determined solely by composition, temperature, and pressure (10, 11).

The present communication extends these observations to solutions of a water-insoluble dye, Yellow AB (benzeneazo- β -naphthylamine), in numerous detergents and mixtures thereof, in an homologous series of pure soaps, and in a pure hydrogen soap. All experiments are at 25.0°C., unless otherwise stated.

COLLOID STABILIZATION

The phenomenon described is that an aqueous detergent solution will take up a definite amount of dye, either from the solid dye itself or from a solution of the dye in an immiscible non-aqueous solvent, setting up a definite equilibrium, losing a portion of its dye to any less saturated non-aqueous solvent, and taking up more from a more nearly saturated non-aqueous solution. The chief non-aqueous solvents used were toluene and benzene. Freezing point measurements show that the dye exists as simple molecules in the benzene solution (molecular weight: theoretical value, 247; value found, 245). A detergent solution, which is originally clear in the ultramicroscope, on taking up dye is still clear in the microscope, but is full of particles visible in the ultramicroscope. In extremely dilute (a few ten-thousandths normal) solutions of a hydrogen soap, laurylsulfonic

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² Lever Brothers Company Soap Fellow.

acid, a small per cent of the particles are so large that they may be centrifuged out in a Swedish "angle" centrifuge. They pass through filter paper. Less dilute solutions are clear and transparent. They are still full of smaller particles, as shown by the ultramicroscope, but none can be centrifuged out. Interesting parallels are found in some of the observations of von Kúthy and Banga (6).

The dye is brought into aqueous solution by spontaneous colloid stabilization. Its amount increases with increasing concentration of the detergent or stabilizing colloid. However, it is a remarkable and distinctive fact that a given weight of detergent takes up more dye when it is most diluted. Thus, so far as our studies have gone, the protective solvent power of a definite amount of a stabilizing colloid is increased by addition of the non-solvent water. This distinguishes the formation of stabilized colloid from the typical cases of Neuberg's "hydrotrophy" or increased solubility in water (3, 4, 6, 8, 13, 17), occurring in general without the presence or formation of any colloid.

Again the phenomenon of colloid stabilization is different from "protective action" or "peptization" of preëxisting particles in suspensions or gels.

THE FORMATION OF STABILIZED COLLOID DYE IN AQUEOUS LAURYL SULFONIC ACID

The especially pure laurylsulfonic acid, $C_{12}H_{25}SO_3H$, was prepared by Dr. Marie Louise Koenig by the method of Noller and Gordon (14).

The spontaneous colloid stabilization of Yellow AB in aqueous solutions of laurylsulfonic acid was determined in two series of experiments. In the first series a small weighed amount of solid dye was shaken with the aqueous detergent. The undissolved dye was filtered off in a Jena No. 4 sintered-glass Gooch crucible and the excess of undissolved dye weighed after washing and drying at $60^\circ C$. The filtrate was likewise analyzed by repeated extraction with purified benzene, from which the dissolved dye was recovered by evaporation, and weighed. The two analyses agreed.

A second series was carried out because of our fear lest some very fine particles of solid dye had passed through the filter. Solid dye was completely eliminated by the device of using only the solution in toluene. To 100 cc. of a saturated solution of the dye in toluene 10 cc. of toluene was added to obviate the possibility of solid dye separating. The aqueous solution was then exposed to the toluene layer, using the device previously described for determining dye numbers, when an extremely slow swirling motion was given to the system with no possibility of breaking up or mixing the layers. The results of the analyses by extraction and by the colorimeter were then multiplied by 11/10 to represent approximate saturation. No emulsified toluene was visible in the ultramicroscope either

with or without dye. The Yellow AB contained 0.15 per cent by weight of a water-soluble sulfate and chloride. The data are given in table 1 and figure 1. The solubility of Yellow AB in pure water is so very slight that it is insufficient to color the water even faintly, far less to weigh or

TABLE 1

The solubility of Yellow AB in aqueous laurylsulfonic acid at 25°C., in milligrams of dye per 100 cc. of solution

CONCENTRATION OF RSO_3H	FIRST SERIES			SECOND SERIES		
	Solubility		Grams of dye per gram of soap	Solubility		Grams of dye per gram of soap
	By weight	By extraction		By extraction	By color	
N_W	mg.	mg.	grams	mg.	mg.	grams
0.00052	6	5	0.4-0.5	5.5		0.42
0.00104	8	7	0.27-0.31	7.7		0.30
0.0052	24	23	0.18	24	23	0.18
0.0052	25	23	0.18			
0.0104	46	43	0.173	42	44	0.17
0.052	244	241	0.186	215	225	0.17
0.052	250	230	0.184			
0.104	640	650	0.245	671	638	0.251
0.52	2150	2130	0.165	1804	1919	0.143

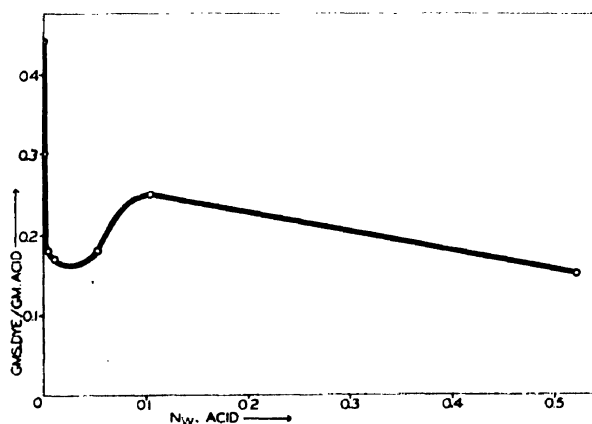


FIG. 1. Solubility of Yellow AB in laurylsulfonic acid, in grams of dye per gram of soap.

analyze. It should be noted that, since the molecular weight of the detergent (250.2) is so nearly that of the dye (247), the ratios in grams are equal to the ratios in molecules, as plotted in figure 1. Figure 1 emphasizes that in extreme dilution the detergent is most effective in bringing into stable colloidal solution almost half of its own weight of dye. This is

more remarkable because in extreme dilution most of the detergent itself is certainly not present in colloidal form, but is almost completely ionized. Its conductivity is slightly lowered by dissolving the dye. Hartley agrees that here the detergent is almost wholly ionized, but on the other hand he considers that the taking up of dye is "almost conclusive proof" of the presence of micelles and that the micelles are liquid. The increase in solvent power on dilution may be an important factor in rinsing.

The whole curve resembles the surface tension curve of aqueous laurylsulfonic acid, and the minimum occurs in the same low concentration in each case. The downward slope in the more concentrated solutions in figure 1 corresponds to the general behavior of very numerous detergents, following the purely empirical rule of McBain and Woo that the amount of

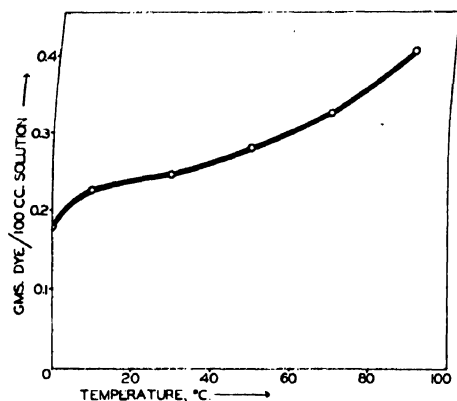


FIG. 2. Solubility of dye in 0.052 *N* laurylsulfonic acid, at temperatures from 0°C. to 90°C.

dye stably dissolved is proportional only to the 2/3 power of the concentration of detergent.

Likewise, the greatly increased solubility of Yellow AB when the temperature of 0.052 *N* laurylsulfonic acid is raised from 0°C. to 90°C. shows that the effect bears surprisingly little relation to the amount of colloid originally in the laurylsulfonic acid. This is largely colloidal at 0°C. and mostly crystalloidal at 90°C. The data are given in figure 2.

As regards other detergents, the solubility of Yellow AB in a 1 per cent, or 0.0226 *N*, solution of pure sodium sulfonate of dioctyl succinic ester (molecular weight 442) is 451 mg. per 100 cc. (determined by weight), 449 mg. (determined by extraction), or 0.45 of the weight of the detergent. Either in weight ratio or mole ratio this is much more than in laurylsulfonic acid of the same concentration. The commercial product, supposedly 99.6 per cent pure, twice gave a value of 449 mg. per 100 cc.

The solubility in 1 per cent "aliphatic ester sulfate" was 497.5 mg.

(determined by weight) and 496.1 (determined by extraction). That calculated from the empirical dye number formula is 496.1, showing the useful range of this merely empirical and certainly not general formula.

The solubility in a 0.0107 per cent solution of a commercial "75 per cent Turkey red oil" was 13.0 mg. (determined by weight), 12.8 mg. (determined by colorimeter), and 12.0 mg. (determined by extraction), which is much more than the weight of the Turkey red oil. (The dye number in this concentration, which is approximately only 0.0005 *N*, is at least 3.) A solution of twice this concentration dissolved 21.0 mg. (determined by weight), 21.0 mg. (determined by colorimeter), and 20.0 mg. (determined by extraction), about equal to the weight of the impure Turkey red oil. Without addition of water the solubility was 7.32 g., in 5 per cent solution it was 0.988 g., and in 1 per cent solution it was 0.291 g. (11), so that the proportionate weight of dye increases very greatly down to extreme dilution of the Turkey red oil.

The following solubilities were determined in 1 per cent aqueous solution: ethyl alcohol, 0.2 mg. (determined by weight), 0.3 mg. (determined by extraction); amyl alcohol, 0.0 mg. (determined by weight), no color; diethylene glycol, 0.1 mg. (determined by extraction), no color; glycerol, 0.0 mg. (determined by extraction), no color. These results are of exceptional interest when compared with the effect on dye numbers tabulated later.

The effect of the presence of 5 per cent Calgon in 1 per cent solution of the Turkey red oil is to change the solubility from 291 mg. to 18 mg. (determined by extraction). In 5 per cent Turkey red oil it is changed from 988 mg. to 296 mg. (determined by extraction). The solubility in 1 per cent Turkey red oil is raised from 291 mg. to 298 mg. by adding 0.2 per cent Calgon.

THE DYE NUMBERS OF THE HOMOLOGOUS SERIES OF SOAPS

Dye numbers are determined (11) by exposing a detergent solution to 2 cc. of toluene containing usually 40 mg. of Yellow AB, for at least 48 hr., avoiding all emulsification. They are expressed as 100*K*, where *K* is the constant from the equation

$$D_{\text{aq.}} = K \cdot D_{\text{tol.}}^{2/3} \cdot S_{\text{aq.}}^{2/3}$$

where *D* is the concentration of dye in the aqueous and toluene layers, respectively, and *S* is the concentration of the soap or other stabilizing colloid referred to the water present. Concentrations are in grams per 100 g. of solvent, except that for Yellow AB *D*_{tol.} is expressed in grams per 100 cc. of toluene. The dye number so obtained is wholly independent of the previous history of the system and its components, provided that at

least two days have been allowed for equilibrium to be established from either side. In every case the dye number is obtained by approaching equilibrium from both sides; in one experiment always dissolving the dye in the toluene first, and in the other dissolving it in the soap solution first

TABLE 2
Dye numbers, 100K, of the soaps (above C_8)

SOAP	DYE NUMBERS IN SOLUTIONS OF CONCENTRATIONS GIVEN				MEAN
	0.2 per cent	0.5 per cent	1 per cent	5 per cent	
Potassium nonylate, C_9	(0.38)	0.268	0.261	0.257	0.265
Potassium caprate, C_{10}	0.809	0.825	0.818	0.820	0.818
Potassium undecate, C_{11}		2.68	2.69		2.68
Potassium laurate, C_{12}	3.58	3.59	3.57	3.55	3.57
Potassium myristate, C_{14}	3.83	3.80	3.84	3.71	3.79
Potassium palmitate, C_{16}	3.74				3.74
Sodium laurate		3.02	3.06		3.04
Potassium oleate			5.80		5.80
Sodium oleate			5.69	5.65	5.67
Sodium abietate			1.16	1.13	1.14
Sodium erucate	5.26				5.26

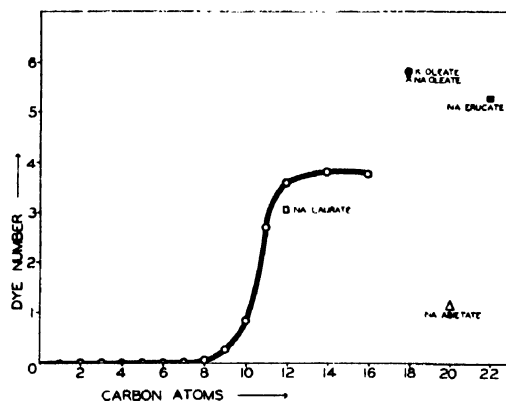


FIG. 3. Dye numbers of potassium salts of saturated fatty acids. □, sodium laurate; △, sodium abietate; ⊙, potassium oleate; ×, sodium oleate; ■, sodium erucate.

before exposing it to the other phase. The results almost always agreed within a few per cent, and the mean was taken to calculate the dye number. The dye number is 0 in the absence of stabilizing colloid. It is likewise 0 for an unstable hydrosol.

The dye number is 0 for the potassium salts of the fatty acids from the

formate through the acetate, propionate, butyrate, valerate, and caproate to the heptylate inclusive, whether in 1 per cent or 5 per cent solution. Potassium octoate (caprylate) in 5 per cent solution gives a value 0.05, but for 1 per cent, 0.5 per cent, and 0.2 per cent solutions it is 0. The dye numbers for the higher soaps are given in table 2 and in figure 3. All these soaps and salts were prepared from Kahlbaum's and the East-

TABLE 3

Dye numbers of commercial soaps or those from technical ingredients

1 per cent solutions

SOAPS	DYE NUMBERS	SOAPS	DYE NUMBERS
Oleic acid soap.....	4.25	Flakes "A".....	4.70
Palm oil soap.....	4.73	Flakes "B".....	3.89
Tallow soap.....	8.50	Powder "A".....	5.25
Olive oil soap.....	6.98	Powder "B".....	3.28
Stearic acid soap.....	5.99	Powder "C".....	3.54
Potassium coconut oil soap (dried).....	4.80	Powder "D".....	7.55

TABLE 4

Dye numbers of sulfonated oils

SULFONATED OILS	DYE NUMBERS		
	From 1 per cent solution	From 5 per cent solution	Mean
"75 per cent Turkey red oil".....	6.22	5.96	6.09
"Sodium sulforicinate".....	4.12	4.11	4.12
65 per cent sulfonated castor oil, of 8 per cent SO ₃	6.06	5.88	5.97
82 per cent sulfonated castor oil, of 8 per cent SO ₃	5.97	5.49	5.73
Equal mixture of last two.....	6.01	5.54	5.72
70 per cent sulfonated castor oil, of 4.3 per cent SO ₃ ..	4.40	4.60	4.50
Sulfonated castor oil "A".....	2.39	2.39	2.39
Sulfonated castor oil "B".....	2.17	2.07	2.12
Sulfonated castor oil "C".....	6.03		6.03
"Highly sulfonated olive oil".....	6.18	6.24	6.21
48 per cent sulfonated castor oil, of 32.5 per cent SO ₃ ..	5.16	5.14	5.15*

* Corrected for moisture of original, gives dye number 8.4.

man Kodak Company's purest materials, except that the oleic acid was made by British Drug Houses by Lapworth's method; the sodium abietate was an especially pure specimen prepared by E. I. du Pont de Nemours and Company and preserved under alcohol; the decoic acid was made by Dr. S. Lepowsky, and the undecoic acid by Dr. C. R. Noller.

For comparison with the pure chemicals in table 2, we have given in

TABLE 5
Effect of added substances upon dye numbers

SOLUTIONS USED	DYE NUMBERS
1 per cent potassium oleate	5.8
+ 1 per cent sodium chloride	3.05
+ 5 per cent sodium chloride	0
+ 1 per cent potassium carbonate	8.5
+ 0.1 per cent Calgon	6.0
+ 0.2 per cent Calgon	6.9
+ 0.5 per cent Calgon	5.2
+ 1 per cent Calgon	3.9
+ 5 per cent Calgon	0*
+ 0.2 per cent trisodium phosphate†	6.1
+ 1 per cent trisodium phosphate	6.9
+ 5 per cent trisodium phosphate	6.0
+ 5 per cent sodium metasilicate	3.9
+ 5 per cent sodium silicate (2.4)	7.0
+ 5 per cent sodium silicate (3.2)	7.0
+ 0.5 per cent gum tragacanth	5.2
1 per cent potassium laurate	3.57
+ 1 per cent sodium carbonate	4.20
1 per cent "75 per cent Turkey red oil"	6.1
+ 1 per cent sodium chloride	2.0
+ 5 per cent sodium chloride	0
+ 1 per cent sodium carbonate	8.5
+ 0.1 per cent Calgon	6.0
+ 0.2 per cent Calgon	6.9
+ 0.5 per cent Calgon	6.0
+ 1 per cent Calgon	4.2
+ 5 per cent Calgon	0*
+ 0.2 per cent trisodium phosphate	6.03
+ 1 per cent trisodium phosphate	5.94
+ 5 per cent trisodium phosphate	5.25
+ 5 per cent sodium metasilicate	6.1
+ 5 per cent sodium silicate (2.4)	8.6
+ 5 per cent sodium silicate (3.2)	10.6
+ 0.5 per cent gum tragacanth	6.0
5 per cent "75 per cent Turkey red oil"	6.0
+ 5 per cent diethylene glycol	9.0
+ 5 per cent glycerol	8.8
+ 1 per cent glycerol	8.5
+ 5 per cent ethyl alcohol	1.44
+ 5 per cent diethyl ether	0.92

* Salted out.

† $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$.

TABLE 5—*Concluded*

SOLUTION USED	DYE NUMBERS WHEN PER CENT OF SILICATE ADDED IS		
	5 per cent	1 per cent	0.2 per cent
1 per cent Turkey red oil (dye number = 6.1)			
+ silicate "S" (3.91).....	10.51	6.84	6.08
+ silicate "O" (3.15).....	10.5	6.81	6.01
+ silicate "N" (3.19).....	10.6	6.84	6.03
+ silicate "K" (2.79).....	6.1	6.08	6.01
+ silicate "U" (2.41).....	8.5	6.01	6.00
+ silicate "C" (1.9).....	6.0	6.87	5.99
+ metasilicate (1.0).....	5.2	6.01	6.87

table 3 the dye numbers of five soaps made from single technical materials, kindly supplied by the National Oil Products Company, four commercial soap powders from different makers (one possibly containing a portion of synthetic detergent), two commercial soap flakes, and a potassium coconut oil soap supplied by the Davies-Young Soap Company.

THE DYE NUMBERS OF THE SULFONATED VEGETABLE OILS

In table 4 are listed the dye numbers of sulfonated oils, some of which, like sulfonated olive oil and sulfonated castor oil (Turkey red oil), have been known and used in the dye industry for nearly a century, but whose manufacture has in recent years been improved as regards control and degree of sulfonation. Our thanks are due to the many firms in this and other countries who kindly supplied or obtained for us these and our very varied assortment of detergents. A few were synthesized under the supervision of Dr. C. R. Noller at Stanford University. The dyes were given to us by the Calco Company. In table 4 degree of sulfonation appears to be a minor factor as compared with the dilution of the original material.

SOLUTIONS LACKING DYE NUMBER OR PROTECTIVE SOLVENT POWER

The following substances leave water a complete non-solvent for Yellow AB when they are added to the extent of 1 or 5 per cent, and their dye number is 0: sodium alginate (pure), sodium silicates (all), sodium hexametaphosphate (Calgon), trisodium phosphate, gum tragacanth, ethyl alcohol, amyl alcohol, diethylene glycol, glycerol, casein. It is all the more interesting that some of these substances enhance the dye numbers of Turkey red oil and of potassium oleate.

EFFECT OF ADDED SUBSTANCES UPON DYE NUMBERS

The experiments in table 5 were performed by adding various substances to solutions originally containing either 1 per cent of potassium oleate or 1 or 5 per cent of "75 per cent Turkey red oil." The effect of admixtures in enhancing the formation of stabilized colloid is noteworthy,

TABLE 6
Dye numbers of synthetic electrolytic detergents

DETERGENTS	DYE NUMBERS		
	From 1 per cent solution	From 5 per cent solution	Mean
Trimethyldodecylammonium bromide (pure)	6.74	6.72	6.73
A technical cationic active detergent	2.07		2.07
A quaternary ammonium base	1.16	1.12	1.14
Another quaternary ammonium base	1.22	1.21	1.22
An imidazole compound	1.26	1.22	1.24
Sodium alkylated naphthalenesulfonate	3.28		3.28
Sodium monosulfonate of dioctyl succinate (pure) . . .	8.15*		8.15*
+ 1 per cent glycerol	10.23		10.23
+ 1 per cent diethylene glycol	10.30		10.30
Sodium secondary-tetradecyl sulfate		1.47	1.47
Sodium secondary-octyl sulfate		0.13	0.13
Sodium secondary-heptadecyl sulfate	0.39	0.38	0.38
An Igepon product	6.85	6.92	6.89
Technical sodium oleyl sulfate	4.16	4.14	4.15
Technical sodium steryl sulfate	9.74	9.81	9.78
Technical sodium lauryl sulfate	3.94	3.90	3.92
Technical sodium octyl sulfate	2.96	2.94	2.95
Sodium lauryl sulfate	5.06	5.18	5.12
Ammonium lauryl sulfate	5.93	6.04	5.99
Diethanolamine coconut oil dimethyl sulfate	3.89	3.65	3.8
A sulfated fatty alcohol	5.99	5.44	5.7
A technical alkyl sulfate powder	4.21		4.21

* Calculated from the solubility of the dye in 1 per cent solution (0.449 g. per 100 cc.) is 8.01; dye numbers with 1 per cent and toluene tend to give a higher result, and the experiment with 5 per cent is precluded by the complete emulsification of the toluene.

even when some alone exhibit no dye numbers and have no hydrotropic actions in the dilutions considered. This is especially clear with such added substance as diethylene glycol and glycerol, as well as some of the sodium silicates. The addition of small quantities of Calgon is favorable, but large additions spoil the detergent.

DYE NUMBERS OF SYNTHETIC DETERGENTS

The names given for the synthetic detergents listed in table 6 are those of the pure chemical or of the main constituent when thus stated and

supplied by the maker. In many cases only an indication of the type of a commercial product can be given. The proportion of active material and of other materials in the technical preparations varies greatly and in many cases is unknown to us. Some of these data are included from a previous communication (11). Where the technical constituent is diluted or where it contains also salts or substances such as alcohol, the dye number suffers accordingly and the value recorded here is too low.

DETERGENTS THAT ARE NON-ELECTROLYTES

Colloid stabilization may be brought about by substances that are very different from the soaps or other salts, acids or bases, such as have been

TABLE 7
Dye numbers of non-electrolytic detergents

DETERGENTS	DYE NUMBERS		
	From 1 per cent solution	From 5 per cent solution	Mean
Nonyl glucoside (pure)	5.24		5.24
Synthetic non-electrolytic polymer	6.60	6.58	6.59
Another non-electrolytic polymer		7.33	7.33
Polyglycerol ester		4.15	4.15
Polyhydroxyether, technical		3.62	3.62
A polyether alcohol	1.81		1.81
Polyethylene glycol condensate (?)	5.97	5.20	5.63
Condensate of C ₁₈ alcohol and ethylene oxide	1.96		1.96
Another condensate or polymer	1.89		1.89
Diglycol laurate	5.63	5.63	5.63
Saponin Quillaia, Merck, purified	0.54	0.54	0.54
Diethanolamine fatty acid	4.21	3.53	3.9
Diethanolamine coconut oil	6.01	5.39	5.7
Another diethanolamine coconut oil	5.97	5.49	5.7
Diethanolamine oleic acid	3.86	3.66	3.8
Diethanolamine stearic acid	3.57	3.62	3.6

enumerated in the foregoing tables. It is of very great interest that detergent power is independent of both dissociation and hydrolysis, although both of these affect the electrolytic detergents. The non-electrolytic detergents cover the same range of dye numbers as the electrolytic ones. Table 7 lists a few of these.

DISCUSSION

Considerations of space preclude any detailed discussion here. The newer trend of the results is quite clearly in the further direction of surmising that a stabilized particle, that is, an unstable particle merely coated with stabilizing agent, may possibly be stable as compared with the sepa-

rate constituents of which it is composed. This has not yet been proven. However, in the cases here studied it seems probable that, especially in very dilute systems, there is comparatively little stabilizing agent as compared with the insoluble stabilized material. This would lead to the point of view that the molecules of dye associate statistically to particles whose formation is less and less probable as the size increases, but once formed are stabilized by the protective colloid. This presents the conception of a statistical equilibrium.

This paper deals only with proven true reversible equilibria, reached equally from both sides. It is thus distinguished from the experiments of Pickering (15), Bailey (1), Lester Smith (16), Hartley (5), and Lawrence (7), where the usual mechanisms for producing unstable von Weimarn types of sols and emulsions are not guarded against and in many cases are certainly operative; these have long been the usual methods of exceeding equilibrium concentrations.

The present results deal only with moderately dilute systems, and not with the exceedingly complex relations observed in concentrated systems illustrated by the phase rule diagrams of Booth (2) or of Weichherz (18), or with the very concentrated systems in which hydrotropy is so often studied (such as 75 to 250 per cent sulfosalicylic acid).

A detergent might almost be defined as a substance which achieves in very dilute solution a solvent action comparable to that of a highly concentrated organic solvent.

It must again be emphasized that the $2/3$ power rule is valid only over a limited, moderately dilute range. It serves as a reminder that the proportion of dye to Turkey red oil is eighteen times greater in extreme dilution than in pure Turkey red oil itself. The solubility of an azobenzene dye was likewise found by Hartley and Miss Parsons to be fivefold more in a given amount of paraffin-chain salt present than in an equal weight of pure hexadecane. The facts here recorded for these numerous detergents do not accord with the interpretations suggested by Hartley (5) and Lawrence (7).

The $2/3$ power rule for these detergents may, as shown by calculations of Dr. R. D. Vold and Dr. M. J. Vold, equally well be replaced by a formula based upon calculations of Meyer and van der Wyk (12), assuming that particles are built up stepwise, each step (the addition of one more molecule) involving the same energy, provided that it is further assumed that each particle, independent of size, has the same average power of stabilizing a molecule of dye within the detergent solution. This, like the original calculations of Meyer and van der Wyk, is an interesting opposite extreme from the views of Hartley and Lawrence.

It should be emphasized again that the dye numbers and the dye solubilities measure one, but only one, of the factors involved in detergent

action. Further work is needed with systems including fabrics, where dye and detergent compete for the surface of the fabric as well as for each other.

SUMMARY

1. The spontaneous formation of stabilized colloid involving true reversible equilibrium has been further studied.

2. The colloid stabilization appears to be more closely related to the surface activity than to the colloidal nature of the detergent.

3. Dye numbers of many types of modern and synthetic detergents, including pure soaps and other compounds as well as commercial products, have been measured.

4. Detergents that are anion-active like soaps and sulfonates, cation-active like substituted ammonium derivatives, and, most interestingly, non-electrolytic detergents cover the same range of dye numbers.

5. Blends and mixtures, even with materials which possess zero dye number, such as silicates and phosphates, may noticeably enhance the dye numbers of detergents.

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THE MICROSCOPIC STRUCTURE OF PLANT CELL MEMBRANES IN RELATION TO THE MICELLAR HYPOTHESIS¹

WANDA K. FARR

Cellulose Department, Chemical Foundation, Boyce Thompson Institute, Yonkers, New York

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The invention of the compound microscope (7) by the Janssens in 1590 marked the opening of a new era in biological research. Before the close of the seventeenth century, the first important observations of the tissue structure of both plants and animals had been made by Hooke (13), von Leeuwenhoek (17), Grew (12), and Malpighii (20). During the eighteenth century there were few additions to the findings of these pioneers. The impetus to microscopic study which came with the nineteenth century was linked inextricably with marked improvements in the microscopes themselves (29).

Before 1820 the work of Mirbel (22), Treviranus (38), Link (18), and Rudolphi (31) had helped to create an active interest both in England and on the continent. The observations in the botanical laboratory of Schleiden (32) in Jena and in the zoological laboratory of Schwann (34) in Berlin were summarized in 1838 with the announcement that "All organized structures are composed of essentially similar units, namely cells." It is well known to those who are familiar with the development of the biological sciences that this recognition of the universal cellular structure of plants and animals was shared with other contemporary workers (30).

In the living plant cells there are visible two distinctly different parts: the delicate, more or less viscous protoplast, and the comparatively rigid cell membrane which surrounds it. The general organization and function of the protoplast presents problems of the greatest difficulty. Its appearance is constantly changing, and one hundred years ago but little was known of the cellular changes which accompany metabolic and reproductive processes. Cell membranes are more stable, and it is not surprising to find the earliest interest directed toward a more complete understanding of their microscopic structure and composition.

The chemical studies of Payen (27) demonstrated in 1842 that the

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membrane substance of cells from all parts of the plant kingdom, when purified from foreign deposits, exhibits the same composition in terms of relative proportions of carbon, hydrogen, and oxygen. He found also that it assumes a blue color in the presence of iodine and sulfuric acid. He named this membrane material "cellulose."

Concurrently the finer physical structure of certain plant cell membranes was described by von Mohl (23), Schleiden (33), Agardh (1), and others who had observed that they are made up of fine fibrils of uniform diameter. These fibrils, arranged in crossed spirals, have become familiar objects in the many published illustrations of the swollen membranes of cotton fibers (plate I, figure 2).

By means of the polarizing microscopes then available in many laboratories, it was learned that the cellulose membranes are doubly refractive (plate I, figure 1). It was for the purpose of explaining this particular phenomenon, and also the swelling behavior of both cell membranes and starch grains, that, in 1858, Carl von Nägeli (24, 25, 26) developed his well-known micellar hypothesis. The crystalline nature of both structures is indicated by their double refraction in polarized light. Nägeli was not able to see individual crystallites, the presence of which is indicated by this double refraction; therefore he stated that they are submicroscopic. In the dry membrane he believed these "micellae" to be nearly contiguous, to occupy almost all of the available space. The membranes, moistened with water or aqueous fluids, were supposed to take up capillary water upon the surfaces of the micellae, in such a way that the crystallites were separated from one another without losing their cohesive force. If the imbibed water were subsequently evaporated, the condition would be reversed and the original state of the dry material resumed.

Ambronn's (2, 3, 4) studies of the orientation of the crystalline cellulose in cell membranes appeared after a considerable lapse of time. His careful and extensive observations in polarized light have shown that the long axes of the crystallites are arranged parallel to the long axis of the fibril and not necessarily parallel to the long axis of the fiber itself. No finer subdivisions of the fibril were visible to him and he based his interpretations, therefore, upon the assumption that the fibrils are composed of crystalline micellae. His publications have furnished an abundance of data which are in excellent form to be correlated directly with results from the more recently developed method of crystalline analysis,—x-ray diffraction. Ambronn's revival of the micellar hypothesis has played an important part in the widespread use of this theory by x-ray chemists in the interpretation of the diffraction patterns of cell membrane materials.

These studies of orientation by means of polarized light and x-ray diffraction have been supplemented more recently by observations of fibril orientation in ordinary light (28). The high degree of correlation in the

results obtained with the three methods has established Ambronn's original conclusions concerning orientation beyond any reasonable doubt. It must be kept clearly in mind, however, that in these studies of orientation the x-ray diffraction and polarized light analyses have furnished no direct evidence as to the size of the crystallite itself.

The exact form and size of the crystallite, as well as its behavior in the membrane, have been the source of controversy in many allied fields of research. Physiologists have been constantly reminded of the fact that a plant cell membrane made up entirely of submicroscopic crystalline micellae could not exhibit the observed swelling behavior. The enormous force involved in connection with the first intake of water into their carefully dried samples is of a much greater magnitude than is commonly associated with capillarity. These doubts have been augmented by the observance of the profound changes in cell membranes after treatment with reagents which could not be shown to have affected the cellulose itself. A cell membrane may thus lose all of its natural physical characteristics, be resolved into a fine white powder, and during the process the cellulose x-ray pattern shows no evidence of change except the transition from regular to random orientation (9, 10). In a discussion of the shortcomings of the micellar hypothesis from the viewpoint of the physiologist, Fischer in 1927 presented, in one sense, a real challenge to microscopists (11, pages 327 and 328): "This phenomenon of double refraction shows that such an inner structure must exist. This, however, may be a fallacy; we cannot prove the matter experimentally. We cannot produce such a body made up of diminutive parallel-arranged crystallites and then study with polarized light or x-rays a structure of which we, with full certainty, know that it has this microstructure, because we ourselves have produced it."

To many investigators employing microscopic technique, the physical nature of the cellulose crystallite of the cell membrane has never been a settled issue. In the presence of an accumulating mass of indirect evidence that the cellulose crystallites are in the form of submicroscopic micellae of varying dimensions, their efforts have been directed toward a possible physical disintegration of the cellulose fibril into visible units. Such units, fibrillar or otherwise, must not owe their existence to a chemical degradation of the cellulose. Degradation may be avoided by the use of reagents which do not affect the cellulose itself or, even more satisfactorily, by the dissection of fresh membranes from living plant cells by mechanical means alone.

Early in 1930 a new approach to the problem of fibril structure through dissections of fresh membranes and mild chemical treatments of dried membranes was made in our laboratory. We studied many types of living plant cells from various parts of the plant kingdom during the period of

membrane formation. In 1932, by means of improved optical technique, we observed large numbers of uniform-sized ellipsoid particles in the cytoplasm of these living cells (8). They are remarkably stable physically, and, although diminutive in size ($1.5 \times 1.1 \mu$), lend themselves readily to both optical and microchemical analyses. They are definitely doubly refractive in polarized light; the refractive indices of the moist particles from the living cytoplasm of the cotton fiber are 1.565 lengthwise and 1.530 crosswise; they swell and turn blue in the presence of sulfuric acid and iodine; their combustion analysis yields the following results:

	<i>Theoretical value</i>	<i>Found</i>
Carbon, per cent.....	44.4	44.34; 44.30
Hydrogen, per cent.....	6.17	6.31; 6.29 (no ash)

their x-ray diffraction pattern is that of native cellulose (35); and when treated with 18 per cent sodium hydroxide they give the pattern of mercerized cellulose. In other words, these ellipsoid particles show the characteristic properties of cellulose and were designated by us "cellulose particles."

Although separate and in short chains in the interior of the cell, the cellulose particles, during the period of wall formation, appear in the outer regions of the cytoplasm arranged end to end in orderly single rows (plate II, figure 1). The fibrils thus formed were removed from the living cells for more careful study. It then became clear that each particle in the fibril is coated with a viscous material which functions as a cementing material, holding the particles together to form the fibril and the fibrils, layer upon layer, to form the membrane lamellae.

Membranes of moist cotton fibers from the unopened boll can be disintegrated into fibrils and particles by mechanical treatment alone. The membranes of mature, dried fibers require treatment with weak chemical reagents to bring about a similar degree of membrane disintegration. As the reaction proceeds, the cementing material surrounding the particles is observed microscopically to swell and, in so doing, to push the particles farther apart. Long-continued treatment brings about the removal of the cementing material by the solvent. A short treatment leaves little visible evidence of physical effect upon the membrane. The more specific techniques of staining and viscosity (14, 21) measurements show us, however, that few, if any, of these treatments leave the cementing material unaltered. The significant fact is that membrane disintegration is thus brought about without any measurable indication of cellulose degradation. Physically and chemically the particles themselves show no evidence of alteration. The crystalline cellulose of the plant cell membrane is therefore in the form of diminutive ellipsoid cellulose particles whose behavior

in the process of membrane formation we are able to follow with certainty (plate II, figure 2).

The difficulty of obtaining protoplasm from a cell as small in diameter as a cotton fiber, free from all membrane material, is obvious. A larger cell, the marine alga *Valonia ventricosa*, the diameter of which is often as great as 3 cm., is useful in this connection. Samples of protoplasm, carefully removed with a fine pipet, show the presence of cellulose particles and their arrangement in single rows to form the fibrils of the mature membrane (plate III, figure 1). The mature membrane of *Valonia* shows a variation in the orientation of these fibrils from 60° to 90°. In the samples from the protoplasm, the arrangement, as shown by the x-ray diagram, is random. In the mature membrane the correlation between the measurements of orientation as shown in the photomicrographs and upon the x-ray diffraction pattern is very close (plate III, figure 2).

These observations constitute, therefore, a visible representation of the two fundamental principles which led Nägeli to develop the micellar hypothesis: (1) the presence of crystalline material in the membrane, and (2) the evidence that the crystallites themselves were unaltered during the swelling of the membrane with either water or aqueous fluids. The crystalline material is present in the form of microscopic cellulose particles. During the swelling of the membrane these particles themselves do not react with the water. They are observed to be pushed apart, not through a direct capillary force of the entering fluid, but by the swelling reaction of the colloidal matrix which surrounds each individual particle. The more important difference in the theoretical and the observed conditions is therefore due to the presence of the cementing material, the nature of which enables us to explain the known swelling behavior of cell membranes in its various aspects.

A recently completed survey of nineteenth century contributions to the microscopic structure of plant cells has revealed the fact that many investigators saw and recorded the presence of microscopic particles in the cell membranes. A few of them described their behavior in the cytoplasm during fibril formation and deposition (table 1). The cellulose nature of the particles in the cytoplasm was not recognized. The closest approach to this recognition is indicated in the expressed belief of Wiesner (40, page 66) that they are changed into cellulose after they are deposited in the membrane. Both Strasburger and Wiesner believed that the "microsomes" and "dermatosomes" in the living cytoplasm were protein because they stain yellow with iodine. We now know that this is a surface reaction. The greater number of recorded observations of the formation of cellulose membranes from visible structural units occurred before 1850. The wave of interest in cellular reproduction then turned the activities of most microscopists from cell membranes to the intricacies of nuclear

behavior. This type of study brought with it the new techniques of fixing, embedding, sectioning, and staining. The tissues which were actually observed were usually dead and either successfully or unsuccessfully

TABLE I
Early observations of microscopic particles in cell membranes

AUTHOR	DATE	MATERIAL	METHODS	CONCLUSIONS
Lyngbye (19).....	1819	Algae: <i>Gastri- dium ovale</i> (or <i>Halicys- tis ovalis</i>)	Microscopic	Minute "points" visible in cell membrane; draw- ing indicates arrange- ment of the granular structures described
Link (18).....	1819	Algae: <i>Con- ferva annu- lina</i>	Microscopic	"Granula Minuta" in the membrane
Valentin (39).....	1837	Cell walls	Microscopic	Granules in cytoplasm build cross lines which later become spiral lines of cell membrane
Kützing (16).....	1843	Marine algae	Microscopic	Granules in cytoplasm; very nearly invisible; ellipsoid or spherical, seldom filamentous
Agardh (1).....	1852	Algae	Microscopic	Granules (spheroids) in cytoplasm believed to be beginning of fibrils in cell membrane
Nägeli (24, 25, 26).....	1858	Starch grains	Microscopic	Submicroscopic crystal- line micellae to explain double refraction and swelling phenomena
	1863	Cell walls	Swelling phenom- ena	
Strasburger (37).....	1882	Cell walls	Microscopic	Microscopic protein "mi- crosomes" in "Haut- schicht" play impor- tant rôle in wall thick- ening
Wiesner (40).....	1886	Cell walls Fibrils	Microscopic	Cell walls composed of microscopic cellulose "dermatosomes"
Ambronn (2, 3, 4).....	1892	Cell walls	Microscopic	Cellulose composed of sub- microscopic anisotropic crystalline micellae in orderly arrangement within the fibril
	1925	Fibers		

embalmed. After 1890 many generations of students of cytology passed through their entire period of academic training with only the most casual contact with the techniques required for the study of living cells.

We are now in a position to realize that the earlier workers had two of the most important requisites in the study of the microscopic structure of cell membranes,—namely, well made, properly mounted lenses and fresh, unstained material.

The recorded observations of membrane structure made by Lyngbye (19), a Danish clergyman, in 1819, are worthy of reproduction in this connection (plate IV). The plant, *Gastridium ovale*, which he describes was reclassified in 1901 under the name *Halicystis ovalis*. From the description in table 18 (plate IV, figure 2), which applies to his drawings of the entire plant and enlarged portions of it (plate IV, figure 1), we see that he wrote with assurance, "Particula frondis". In the more detailed description of the plant he says (plate IV, figure 3), "Substantia membranacea, non gelatinosa, sed pro tenuitate tenacissima, sub lente minutissime punctata." The photomicrograph made recently in our own laboratory of the membrane of this same plant has the essential characteristics of this drawing made almost one hundred twenty years earlier,—minute particles in random arrangement (plate IV, figure 4). The x-ray diffraction pattern corroborates this random arrangement and shows, in addition, that the cellulose particles are mercerized (36). A cross section of the membrane shown in plate V, figure 1, shows a degree of orientation produced through the deposition of successive layers of cellulose particles. The microscopic and x-ray results show here, also, a close correlation. The regularity of natural orientation in *Halicystis* is, however, not in the same category with that of *Valonia*. In *Halicystis* the cellulose particles do not form fibrils.

At the meeting of the Cellulose Division of the American Chemical Society in April, 1937, a series of microscopic analyses of plant cell membranes was presented by Bailey, Anderson, and Kerr. These papers now published (5, 6) constitute one of the few recent reports of microscopic evidence in support of the micellar hypothesis. They state that their cross sections of cotton fibers have large numbers of lamellae which, upon the basis of counts and measurements made after swelling, are said to have been as thin as $0.1\ \mu$ in the original state. This width is far below the size of the cellulose particle and, if their interpretations of their preparations were correct, it would be incompatible with the existence in the membrane of cellulose in the form of particles $1.1\ \mu$ in width.

Our own studies of cross sections of cotton fibers in both intermittent and continuous illumination have extended over a period of several years. In the course of that time we have learned how to section mature fibers from a boll, not yet at the stage of natural opening, without any form of infiltration and embedding, have found that only cross sections of 2 to 3 micra in thickness are suitable for studies of the lamellate structure, and have learned that uniform swelling throughout the section depends upon

a straight cut exactly perpendicular to the fiber axis across a "position of extinction" (plate I, figure 3). All measurements, counts, and direct observations show that each lamella is made up of a single layer of cellulose particles. A thin layer of cementing material surrounds each particle and alternates with each lamella.

The number of lamellae in the cross section which we use for experimental purposes (*Gossypium hirsutum*, Super Seven, Strain 4) varies from fiber to fiber, from 4 to 15. A cross section whose membrane width is 13 micra will contain, for instance, 10 to 12 lamellae. From recent series of cross-sectional studies, Dr. F. L. Barrows of our laboratory has found an average lamellar width of 1.09μ in eight hundred thirty cross sections. Fibers from plants grown in continuous light—both sodium vapor and sodium vapor and mercury arc—show no differences in the lamellate structure of their walls from those grown under ordinary conditions in the greenhouse or the field.

Our microscopic results may be summarized graphically with the illustrations in plate VI. There are large variations in shape and width of cross sections of fibers from any given boll (figure 1). The thin cross sections are very delicate and must be swollen with the greatest care. As swelling proceeds, the shape of an oval section is retained and the lumen enlarges as the section enlarges (figure 2). The outer limiting membrane of the fiber which does not swell in cuprammonium hydroxide does not play a part in the swelling behavior of such a thin cross section. As swelling continues, the lamellae become visible (figures 3 and 4). Longer continued treatment with the reagent gelatinizes the cementing material, distorts the lamellate structure, and obscures the separated particles (figure 5). Further addition of cuprammonium hydroxide to the mount helps to remove the swollen cementing material and the disarranged particles are more clearly visible (figure 6).

This description of cross-sectional structure and swelling behavior has no points in common with that reported by Bailey, Anderson, and Kerr (5, 6). They state that the sections should be 10 to 15 micra thick; ours are 2 to 3 micra in thickness. Soon after swelling begins in cuprammonium hydroxide their sections turn inside out so that the outer part of the fiber occupies the former position of the lumen; we have observed no such phenomenon in the swelling of the thin cross sections. The outline of the cross section in their final stages of swelling is shown to be circular, and the diameter of the opening in the center of the section is very small in proportion to the diameter of the cross section itself; our cross sections retain their original outline during swelling and the lumen enlarges progressively as the swelling proceeds. In order either to stop the reaction with the cuprammonium solution or to assist in the reversion of the "growth rings" they exert pressure upon the swollen section; the slightest pressure

upon our cross sections at any stage of swelling produces so much distortion that all of the original tissue structure is destroyed.

The preparation of cross sections of cotton fibers according to the procedures described by Kerr (15) has furnished an explanation of the discrepancies between their results and ours. In cross sections 10 to 15 micra in length the cuticle plays an important rôle during swelling with cuprammonium hydroxide. It is observed to behave in three different ways: (1) The cuticle is rolled back to the center of the section and the swollen structure in outline resembles a sheaf of wheat (plate VII, figures 1 and 2). (2) The cuticle constricts one end of the swelling section and the separating fibrils radiate out from the ring of cuticle as a center. This explains the presence of the cuticle in the center of their "cross section". It is not due, however, to the reversal of the inner and outer portions of a true cross section (plate VII, figures 1 and 3). (3) The cuticle splits in the center and a band of it constricts each end of the swelling fiber section. This produces a lantern-like structure. If these sections begin to swell with their long axes horizontal to the surface of the microscope slide, they quickly tip, upon the curve of their swollen side, to a perpendicular position. This motion evidently has been mistaken for a reversal of the inner and outer portions of a true cross section.

Two or more of these three types of swelling may appear in a single field in the microscope (plate VII, figure 1). Only rarely does one type alone occur. Type 3 is evidently the one selected by Kerr and Anderson to demonstrate the number of "growth rings" in the wall of the fiber. These authors show, however, only the final stage of swelling. When the intermediate stages are followed (plate VIII, figure 1), the crossed fibrils of the surface come clearly into view. If swelling continues without pressure, the section is disintegrated without the appearance of "growth rings" (plate VIII, figure 2). If, however, after the swelling is well begun, pressure is exerted upon the cover glass of the mount, the entire swollen mass is thrown into a series of concentric microscopic ridges with the round of cuticle in the center as a point of origin (plate IX, figure 1). If the lantern-like structure is turned upon its side, both rings of cuticle serve as points of origin and the pressure ridges extend along the side of the lantern (plate IX, figure 2). In plate V, figure 2, this same phenomenon, resulting from pressure upon the swollen membrane of *Halicystis*, perpendicular to its surface, is shown. By a comparison with figure 1 it can be seen that these pressure ridges have no relation to the true lamellae. This represents a microscopic phenomenon which we have found in many different gum-like substances. Gum tragacanth softened in water illustrates this point (plate X). A small mass of foreign material has served in this instance as a point of origin.

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These so-called "growth rings" have, therefore, no relationship to the

true lamellae of the cotton fiber wall. Their number and width have no bearing upon the size of the crystalline units of cellulose and do not constitute evidence against the existence of cellulose particles of the size which we have described.

Anderson and Kerr have also stated that the cellulose particles which we have identified in the cytoplasm of the young cotton fiber are really small plastids containing starch. It is necessary, therefore, that we call attention to the fact that starch is not present in the cotton fiber at any stage of development. Starch is present in the outer integument of the cotton seed during its early stages of development (plate XI, figures 1a and 2). After about 12 days from the date of flowering much of this starch is converted into sugar and used up as food for the developing fibers. The starch in the inner integument (plate XI, figure 1) remains until about the 25th day. It is then gradually converted into sugar, which is used in turn in the development of oil in the embryo. The mature cotton seed contains no starch.

It is scarcely necessary to state that the identification of starch and cellulose is one of the most specific and well-known microchemical differentiations of closely related plant materials. The cellulose particles in the young cotton fiber have two refractive indices (1.565 and 1.530); cotton starch grains have one refractive index (1.518), and the plastid has a refractive index of the order of magnitude of protoplasm itself, not exceeding 1.4. The cellulose particles are remarkably uniform in size; plastids with and without starch grains are noted for their lack of uniformity in size. Particles from the cytoplasm of both cotton fibers and *Valonia* (plate II, figure 1, and plate III, figure 1) give x-ray diffraction patterns of cellulose and not starch. A cell from the inner integument of the cotton seed, at higher magnifications, shows a direct visible comparison of the cellulose particles, which have been formed in the cytoplasm of the living cell and used to build up the membrane, with the starch grains which have remained in the interior of the cell (plate XI, figure 3).

SUMMARY

Microscopic research resulted in the realization in the early part of the nineteenth century that all organized plant and animal structures are composed of essentially similar units, namely cells. Before 1850 many of the microscopic properties of the plant cell membrane had been described. Its double refraction in polarized light indicated the presence of a crystalline compound. Its swelling behavior indicated that the crystallites themselves did not react with the swelling agent. Upon the assumption that the cellulose crystallites were invisible and that in the swollen state of the membrane the reagent had merely brought about a wider spacing of these separate individuals, Nägeli, in 1858, developed the hypothesis

that the plant cell membrane is composed of submicroscopic units to which he gave the name "micellae".

The observed cellulose particles have all of the optical properties in polarized light originally attributed to the crystalline micellae and later ascribed to them in orientation studies, with the exception of size. They are approximately 1 micron in size and therefore microscopically visible, while the micellae were presumably microscopically invisible. Especially significant is the additional observation that the space between the crystallites is not vacant, as Nägeli had believed it to be, but is occupied by a colloidal material having physical and chemical properties very different from those of the crystalline cellulose particles. The presence of this colloidal matrix accounts for an adequate force, not considered in the micellar hypothesis, to explain the unique swelling behavior of plant cell membranes.

A survey of botanical literature reveals the fact that the formation and structure of plant cell membranes from visible structural units was observed independently by many investigators previous to 1890. The failure to recognize the cellulose nature of the particles in the cytoplasm has probably contributed to the obscurity of these data, although it is clear that Wiesner approached this recognition in 1886 from his expressed belief that they change into cellulose after they have been deposited in the membrane.

The remarkable uniformity in size, shape, physical properties, and chemical properties of the cellulose particles from all parts of the plant kingdom indicates that our immediate fields for research are in a more complete study of their different types of orientation and of the nature of the materials with which they are so intimately associated.

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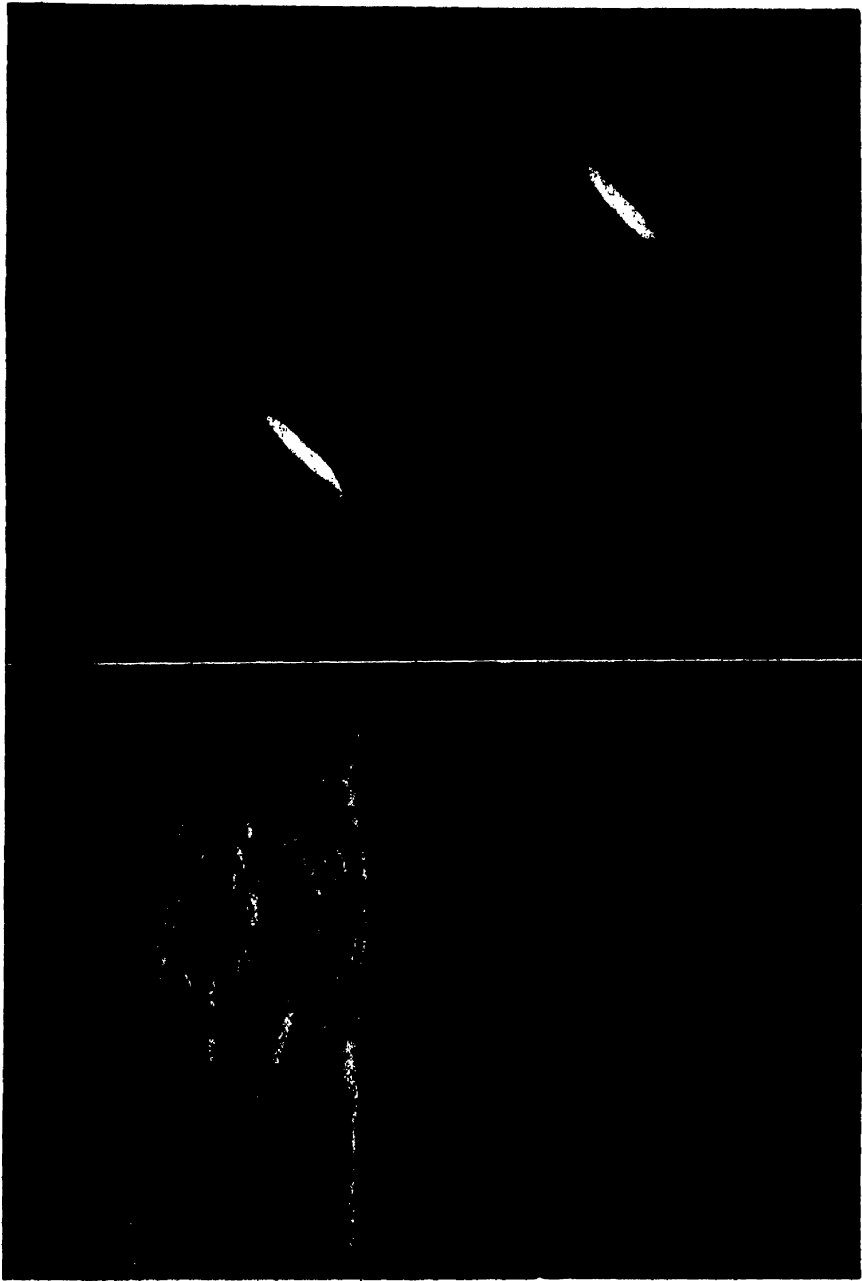
PLATE I²

FIG. 1. Cell membranes of *Spirogyra* sp. show the presence of crystalline material through their double refraction in polarized light ($\times 630$).

FIG. 2. Spiral fibrils in the cell membrane of a cotton fiber (*Gossypium hirsutum*) in polarized light ($\times 900$).

FIG. 3. Fibrils in the cell membrane of the cotton fiber are arranged parallel to the axis at intervals throughout its length and produce "extinction areas" in polarized light ($\times 900$).

² Each plate (I to XI) has been reduced by one-quarter in reproduction.



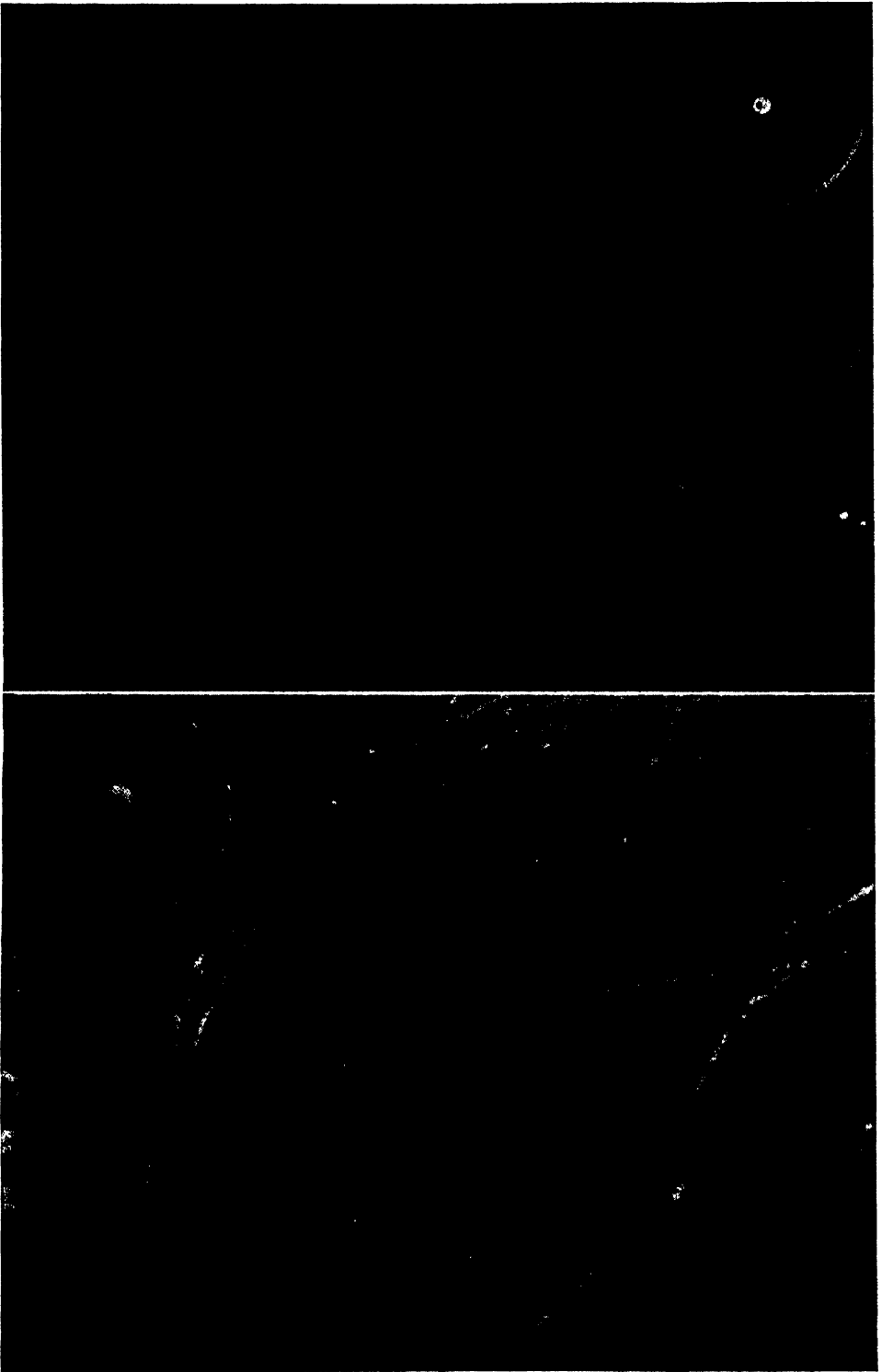


PLATE II

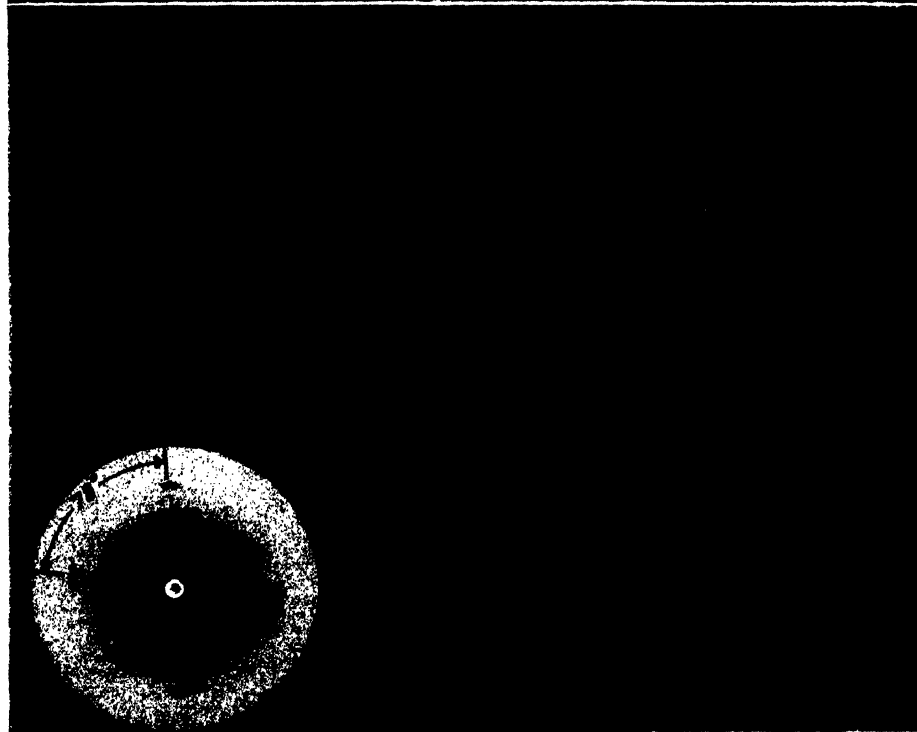
FIG. 1. Cellulose particles, separate and in short chains from the living cotton fiber produce an x-ray diffraction pattern of cellulose in random arrangement ($\times 1500$).

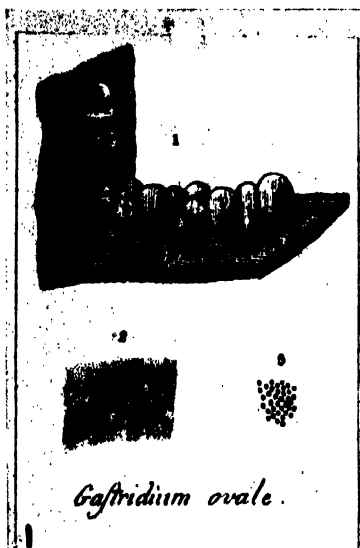
FIG. 2. The cell membrane of a mature cotton fiber produces a diffraction pattern of more regularly oriented cellulose and disintegrates into fibrils and particles identical with those observed in the living cytoplasm ($\times 1380$).

PLATE III

FIG. 1. Cellulose particles and fibrils from the cytoplasm of *Valonia ventricosa* and the x-ray diffraction pattern which they produce when freed from the associated cytoplasmic constituents ($\times 1380$).

FIG. 2. Fibril orientation in the mature membrane of *Valonia ventricosa* is measured directly in the microscope and by means of the x-ray diffraction of the cellulose oriented parallel to the fibril axis ($\times 1350$).





Tab. 18.

- A.1-3. *Gafridium Opuntia* n.m.
- 4. Idem fructiferum n.m.
- 5. Partis frondis seminiferum 2.
- B.1. *Gafridium ovale* ad saxum n.m.
- 2. Partis frondis 3.
- 3. Semina? 1.
- C.1. Fructus *Chorda Fili* 3.
- 2. Idem 1.
- D.1.2. *Chorda Filum γ. trichoides* n.m.
- 3. Ramulus cum fibrillis 5.
- 4. Fibrilla 2.
- E.1. *Chorda Lomentaria* n.m.
- 2. Semina frondi exterius insidentia 1.

Tab. 18. 3. *G. ovale*; fronde tubuloso-lanata, ovali, cinctis, tenaculosis.

Habitat ad infimum collisum litem litoris Favosae, ut ad Qivig, Høyvig &c., rugulis tubulosis adhaerens.

DESC. Radix caesa. Frondes gregalis, ad basin angustato, mox in arminis *Pisi* nativis magnitudinem intumescens, duo tamen haec stirpes longe, apice obtuso, intra massam aquam videretur repleta, itaque distente. Fructus inaequalis. Color viridis. Substantia membranacea, non gelatinosa, sed pro tenuitate elasticam, sub lente minutissima punctata. Aestivo. Chorda non adhaeret.

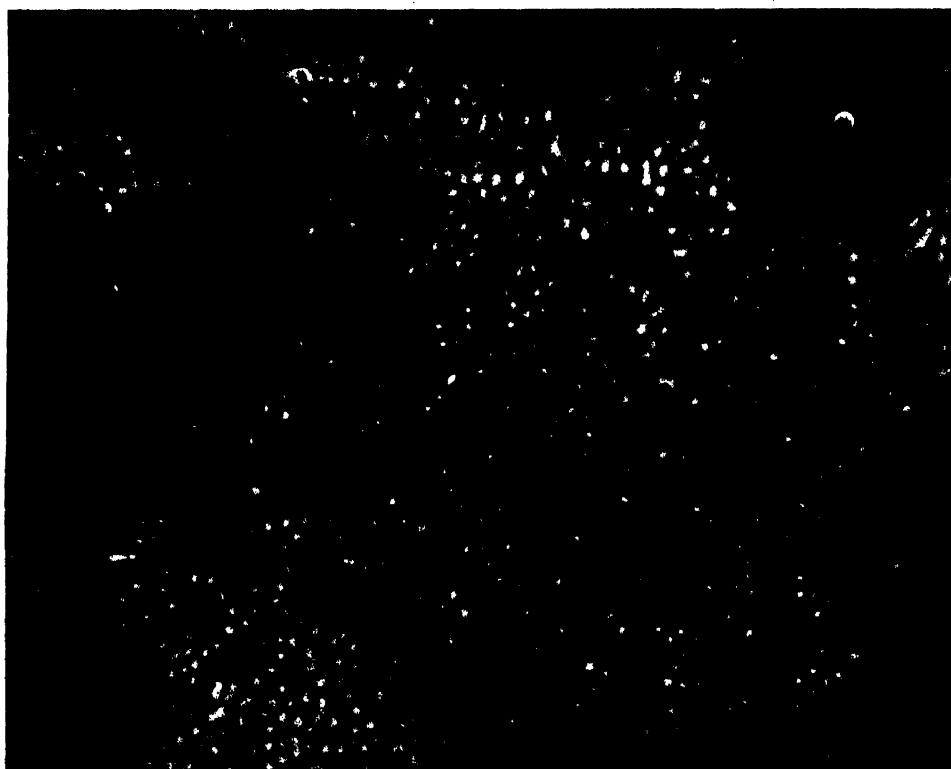


PLATE IV

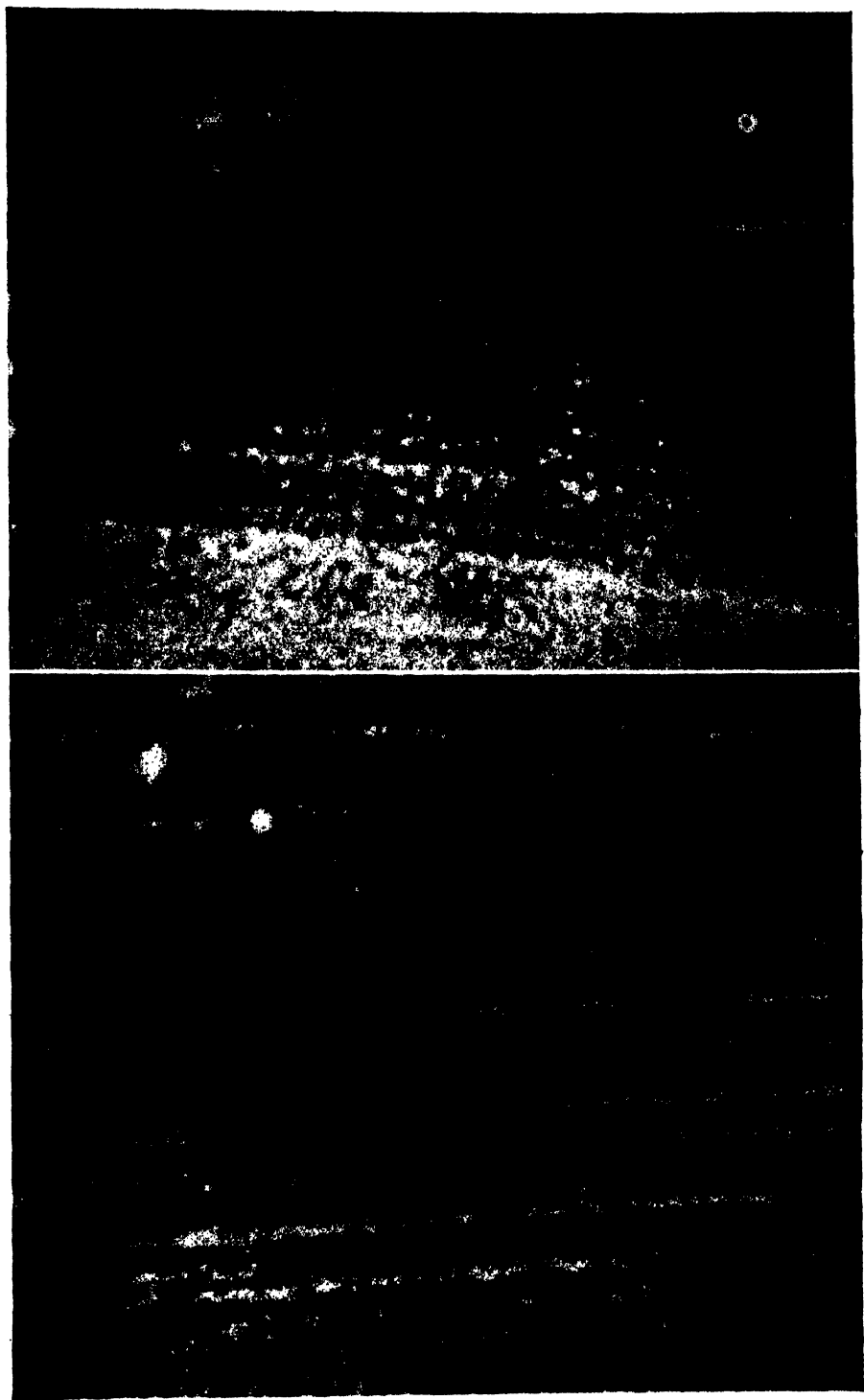
FIGS. 1, 2, and 3. Copies of a plate and text-descriptions from Lynghye (1819). *Gastridium ovale* was renamed *Halicystis ovalis* in 1901.

FIG. 4. Cellulose particles in the inner layer of a membrane of *Halicystis ovalis* in random arrangement. A cluster of dark green plastids is attached to the membrane. The x-ray diagram of the untreated membrane with the beam perpendicular to the surface is that of mercerized cellulose in random arrangement ($\times 1400$).

PLATE V

FIG. 1. A cross section of the membrane of *Halicystis ovalis* shows that single layers of cellulose particles make up the true lamellae ($\times 1120$). The x-ray beam parallel to the surface produces a diffraction pattern of partially oriented, mercerized cellulose.

FIG. 2. Parallel ridges produced by pressure perpendicular to the surface upon the swollen membrane of *Halicystis* ($\times 1120$).



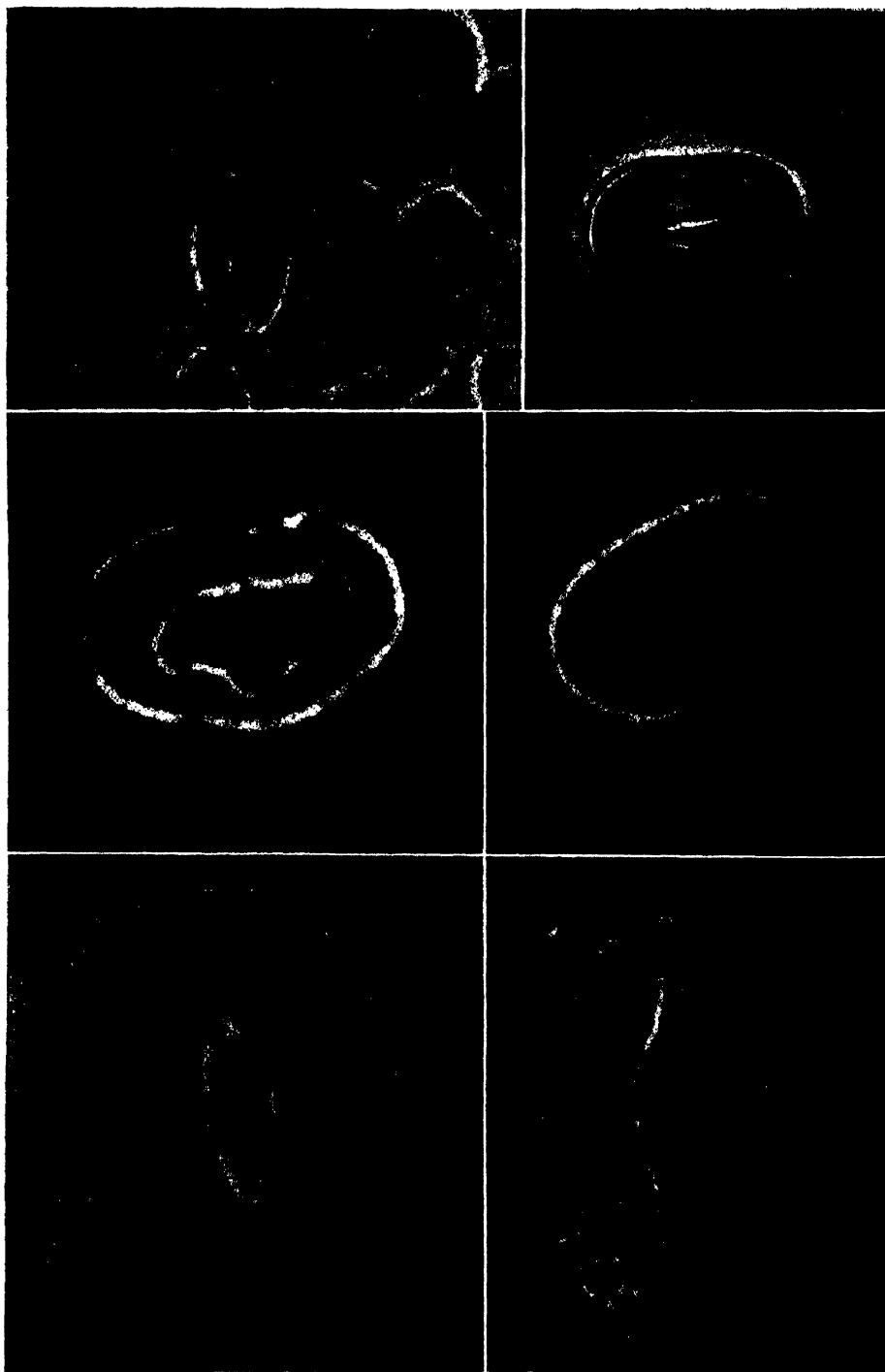


PLATE VI

FIG. 1. Cross sections of cotton fibers, 2 to 3 μ in thickness, show marked variations in size and shape ($\times 920$).

FIG. 2. An early stage of swelling in cuprammonium hydroxide ($\times 920$).

FIG. 3. A later stage of swelling of a section through a region where the fibrils are arranged at an angle with the fiber axis. The lamellae are visible but the swelling of the section is irregular ($\times 1600$).

FIG. 4. A section across a region where the fibrils run parallel to the fiber axis. Swelling is more regular ($\times 1500$).

FIG. 5. In a later stage the rapidly swelling cementing material distorts the lamellae and obscures the particles ($\times 1400$).

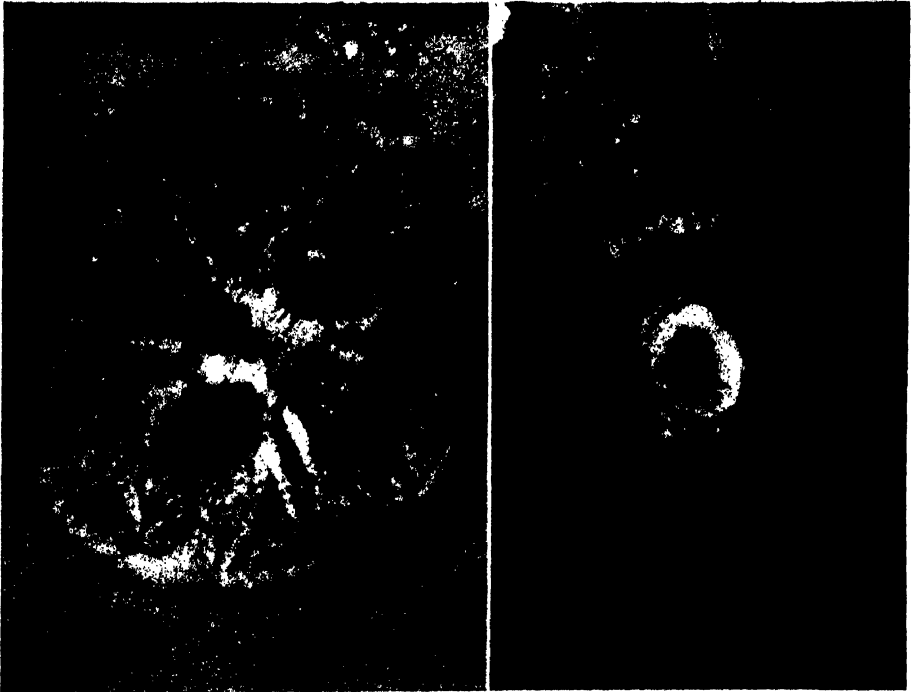
FIG. 6. Continued washing with cuprammonium hydroxide carries away the swollen cementing material and the particles are more clearly visible ($\times 1300$).

PLATE VII

FIG. 1. Early stages of swelling of thick cross sections (10 to 15 μ) of cotton fibers in cuprammonium hydroxide ($\times 1050$). Two examples of type 1 and one of type 2 are shown.

FIG. 2. A late stage of swelling of type 1 ($\times 1030$).

FIG. 3. A late stage of swelling of type 2 ($\times 1000$).



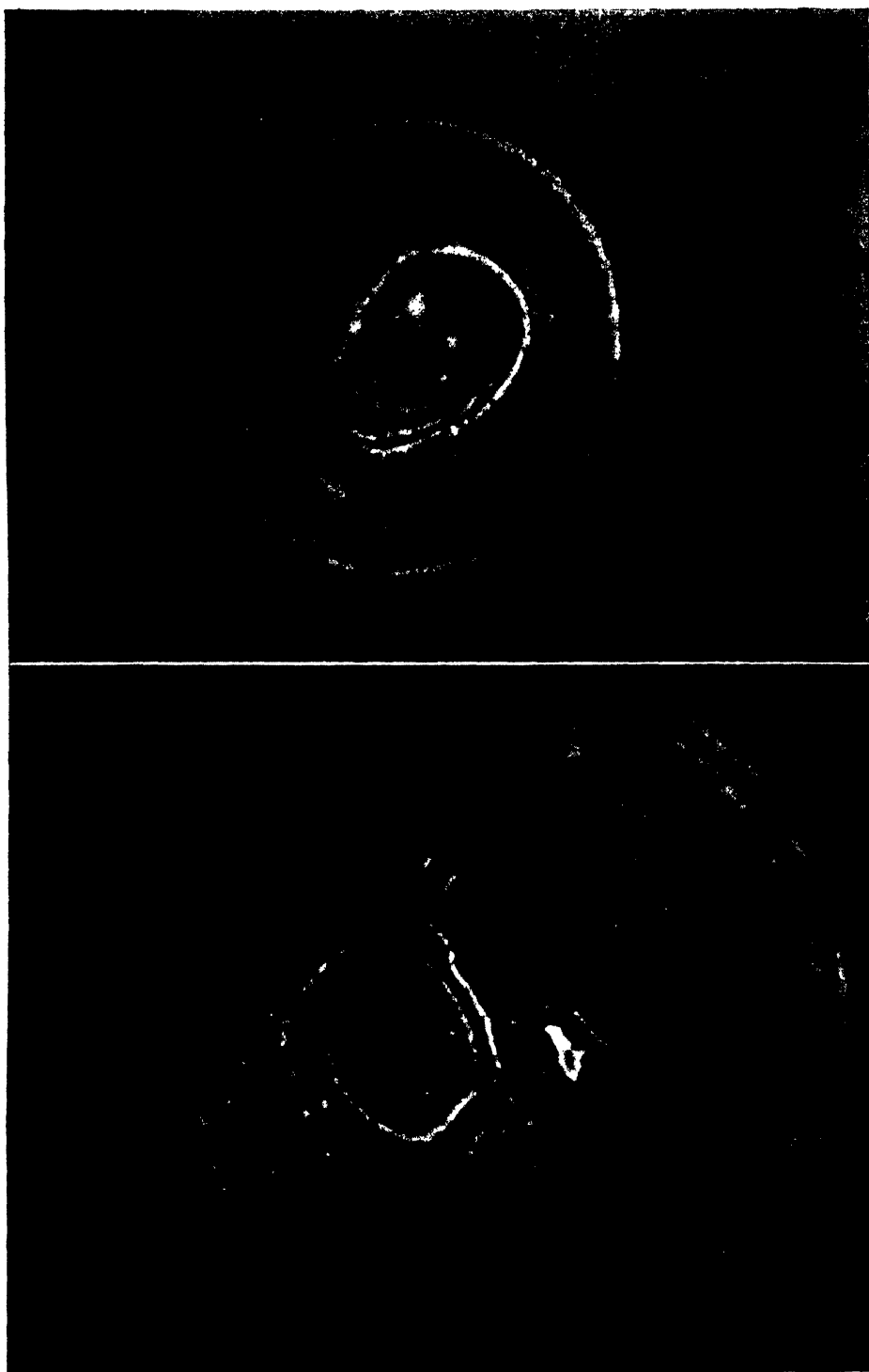


PLATE VIII

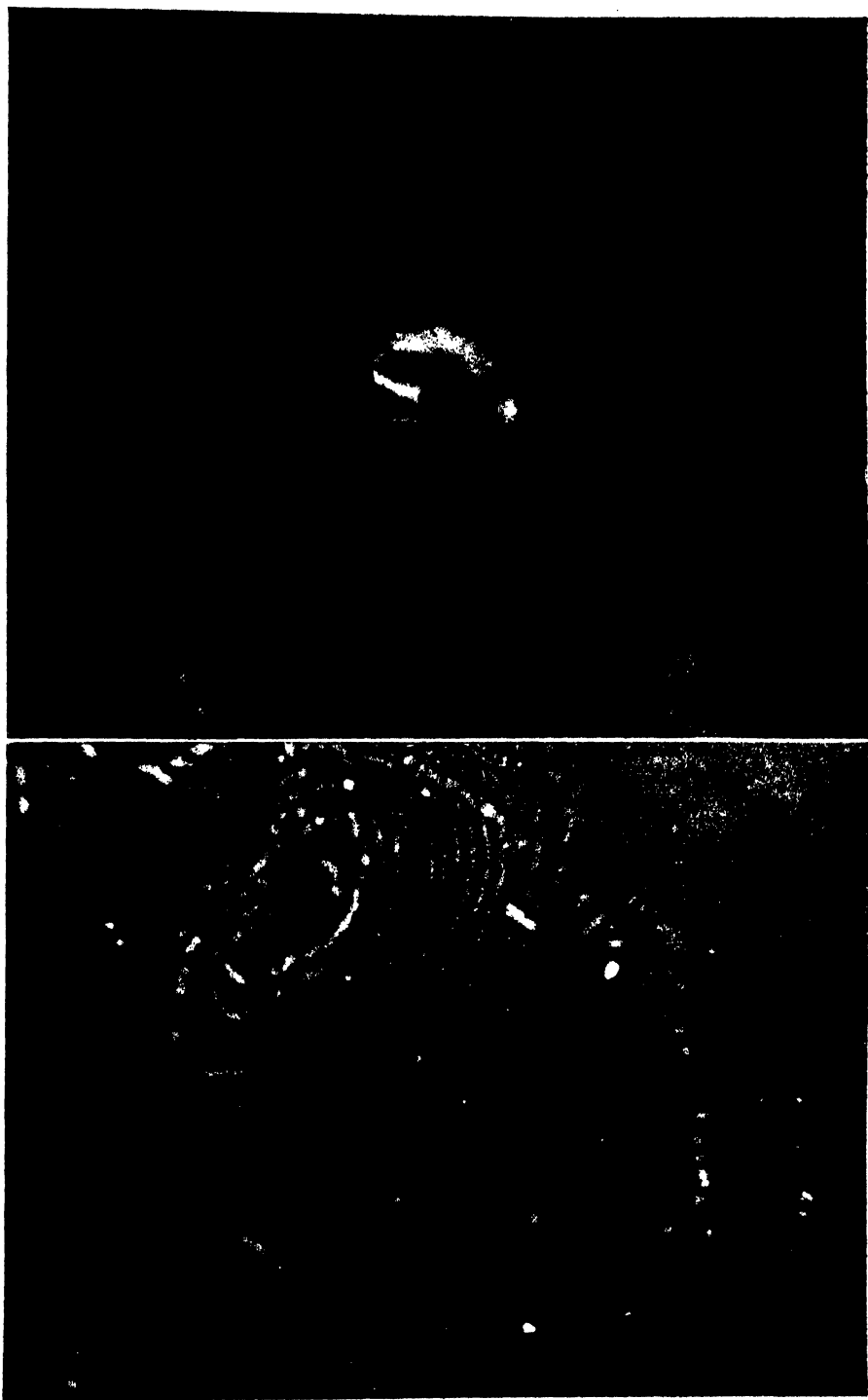
FIG. 1. An early stage of swelling of type 3. Crossed-spiral arrangement of fibrils upon surface of the lantern-like structure are visible ($\times 1050$).

FIG. 2. A late stage of swelling of type 3. No "growth rings" are visible at any stage of swelling without pressure ($\times 1380$); cf. plate IX, figure 1, for pressure artifacts.

PLATE IX

FIG. 1. The effect of pressure upon the cover slip during the swelling of type 3 is to produce a series of concentric "growth rings" with the central ring of cuticle as a point of origin ($\times 1100$).

FIG. 2. When the lantern-like structure is turned upon its side, both rings of cuticle act as points of origin ($\times 700$).



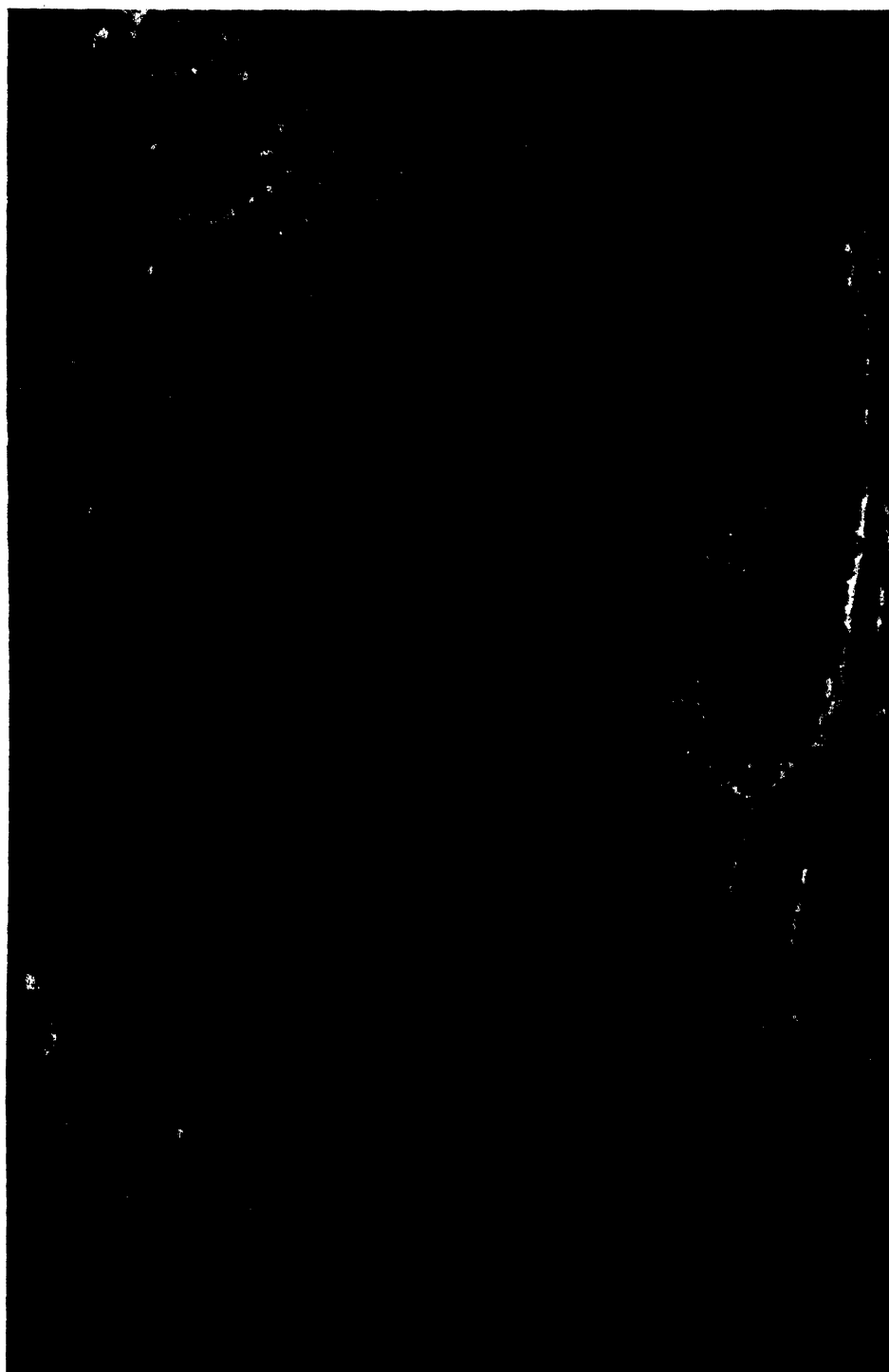


PLATE X

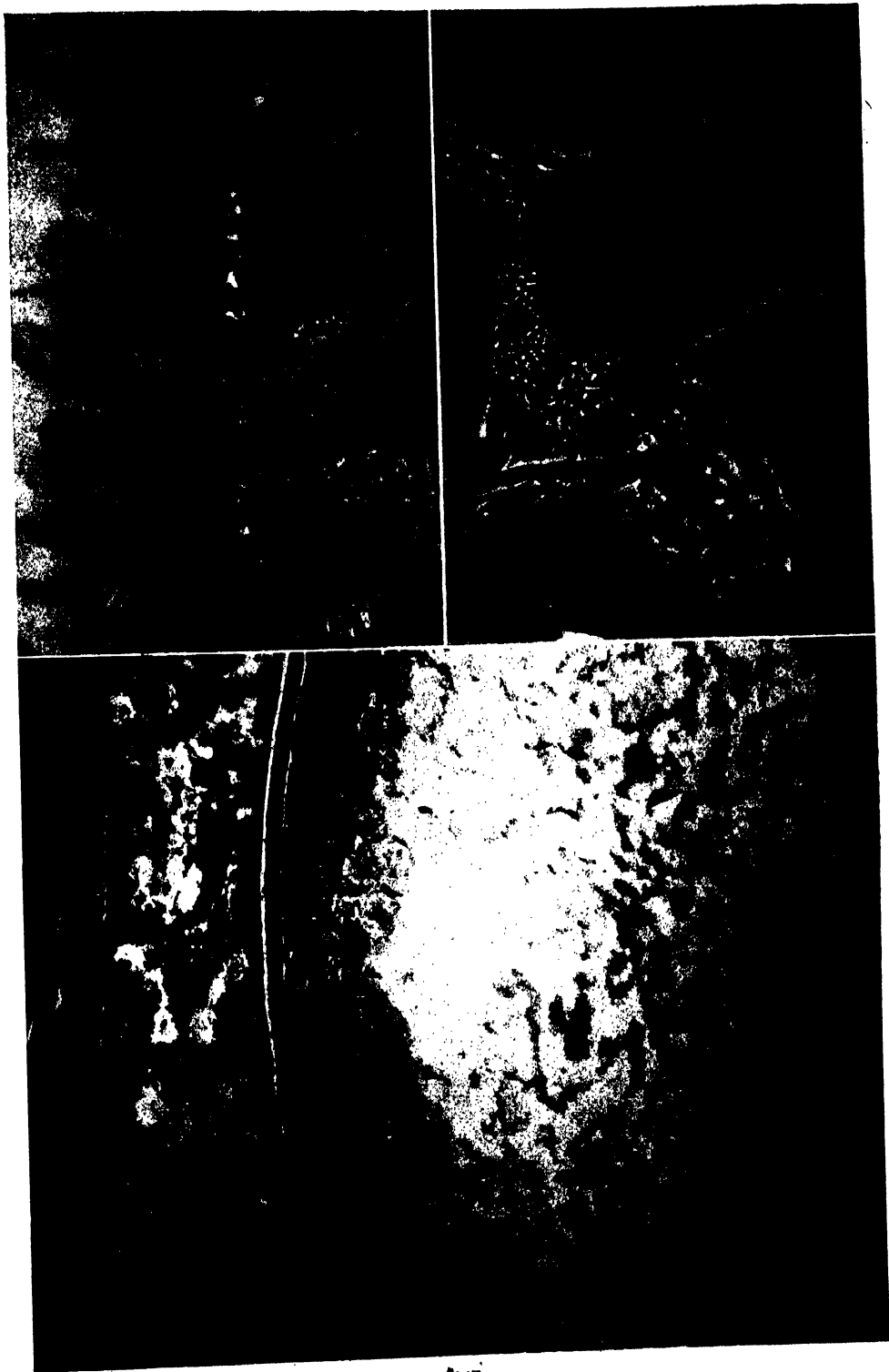
FIG. 1. Gum tragacanth swollen with water. Pressure upon the cover glass produces the parallel ridges radiating out from a small mass of foreign material as a point of origin ($\times 1200$).

PLATE XI

FIG. 1. Polarized light. Cross section of cotton seed showing absence of starch in epidermal cells (a) from which fibers are formed and outer epidermis (c) of inner integument. Starch is present in cells of both outer (b) and inner (d) integument ($\times 743$).

FIG. 2. Starch is absent in young fibers and epidermal cells from which they are formed. Starch grains are being formed in certain cells of the outer integument ($\times 1000$).

FIG. 3. A cross section of cells from the inner integument shows large compound starch grains in the interior of the cells and cellulose particles in the membranes ($\times 1050$).



COMMUNICATION TO THE EDITOR

ATTEMPTS TO PREPARE GREEN GOLD SOLS¹

In attempting to prepare red gold sols by the method suggested by Ostwald,² namely, reduction of gold chloride solution by tannic acid in the presence of potassium carbonate, repeated trials resulted in a sol of a definitely green color. Suspicion pointed to the tannic acid solution which had been on the side-shelf for a long period of time.³ In order to check this point, the experiments were repeated with freshly made solutions of tannic acid, and again with samples of this substance which were (1) allowed to age naturally exposed to air and (2) artificially aged by

TABLE 1

Precipitation experiments on sols

Sample dialyzed 24 hr.; 10 cc. of gold sol taken in each case; time elapsed after addition of electrolyte = 15 min.

ADDED ELECTROLYTE (1 cc.)	RED SOL	GREEN SOL
0.01 <i>N</i> sodium nitrate	Positive	Negative (slight)
0.1 <i>N</i> potassium chloride	Positive	Negative
1.0 <i>N</i> sulfuric acid	Slight	Negative

0.1 *N* sodium hydroxide caused immediate precipitation in both cases.

being bubbled with air for periods of 48 hr. Uniformly the fresh solutions gave the red sol, but both the naturally and artificially aged samples gave the green sols.

These green sols were relatively stable, some of them being preserved in sealed tubes for eight months without coagulation.

A number of precipitation experiments on samples of the red and green sols of comparable strengths was tried. A Tyndall light cone from a brilliant source of illumination was used as the criterion of precipitation. The results of these experiments are summarized in table 1. If the Tyndall effect is listed as positive, the sol had not completely precipitated, while a negative effect signifies that it was optically clear. These results are

¹ Received August 27, 1938.

² See Holmes, *Laboratory Manual of Colloid Chemistry*, p. 32. John Wiley and Sons, Inc., New York (1928).

³ The reference cited in note 2 points out that tannin solutions have a great tendency to develop mold, and suggests the addition of chloroform to prevent it.

typical of many different experiments with varying times and concentrations of added electrolytes, and were essentially the same whether the samples were previously dialyzed or not. In all cases the green gold sol precipitated more completely in a given time than the red.

Attempts were made to separate portions of the aged tannic acid by fractional dialysis. However, when each of these fractions was separately used for reducing gold chloride in a similar manner, green sols invariably resulted. In other words, our attempts to isolate the different possible oxidation products which might be responsible for the two kinds of sols were unsuccessful. Nevertheless, we feel that the experiments were of sufficient interest to justify their being recorded.

HAROLD B. FRIEDMAN.

J. JOE DAVIS, JR.

Department of Chemistry
Georgia School of Technology
Atlanta, Georgia

THE SYSTEM FERRIC OXIDE-SULFUR TRIOXIDE-WATER

F. W. KOERKER¹ AND H. N. CALDERWOOD²

Department of Chemistry, University of Wisconsin, Madison, Wisconsin

Received July 20, 1938

INTRODUCTION

Although the system ferric oxide-sulfur trioxide-water has been studied *in extenso* by many investigators (2), the literature reveals no data for temperatures below 18°C. This paper reports an extension of the study to 15°C., together with some observations on preliminary work at 10°C.

EXPERIMENTAL

Reagents

Analytical grade ferric sulfate and sulfuric acid were used throughout, their purity being determined before use by analysis. The ferric oxide was prepared by the method of Appleby and Wilkes (1). Specially purified distilled water was used for all dilutions.

As the work progressed, it was found that the preliminary mixing of reagents in the form of pastes permitted a closer estimation of the amounts necessary to obtain workable quantities of solid and liquid phases than did simply mixing the solids and liquids.

Method

Weighed samples in sealed glass bottles agitated in a constant-temperature bath for various lengths of time and allowed to settle there were filtered while still in the bath, using a fritted glass filter and the method of Campbell and Slotin (3), and were then analyzed. Disappearance of the liquid phase from the filter frequently required filtration for 6 hr., and even then the solids, although a friable cake, still contained varying amounts of the liquid phase. The minimum time which Appleby and Wilkes report as necessary to establish equilibrium was found applicable to only the basic and neutral regions at 15°C., much longer periods of time being necessary in the acid region. As the system approached the neutral region the liquid phase became deep red, but showed no Tyndall effect with the ultramicroscope until the system was definitely in the basic region.

¹ Present address: Dow Chemical Company, Midland, Michigan.

² Present address: 3105 Cross Street, Madison, Wisconsin.

The data obtained at 10°C. are compiled in table 1, while table 2 contains the results of the work at 15°C., also shown graphically in figure 1.

DISCUSSION OF RESULTS

The results obtained at 10°C. show that the solids from the acid region of the system were more acid in character than those obtained by Appleby and Wilkes at 18°C., and their composition indicates solid solutions of ferric sulfate with sulfuric acid rather than definite compounds. Such an occurrence is very probable, since the freezing points of sulfuric acid and its monohydrate ($\text{H}_2\text{SO}_4 \cdot \text{H}_2\text{O}$) are 10.49°C. and 8.62°C., respectively (4).

TABLE 1

Composition of the solutions, the corresponding residues, and the solid phases in the the system ferric oxide-sulfur trioxide-water at 10°C.

SOLUTION		RESIDUE		SOLID PHASES
Fe_2O_3	SO_3	Fe_2O_3	SO_3	
<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	
2.76	4.12	20.09	30.00	Solid solution
7.32	12.59	29.20	25.80	
16.30	25.88	21.21	34.60	
2.23	16.19	8.38	29.80	$\text{Fe}_2\text{O}_3 \cdot 2.44\text{SO}_3 \cdot 8.65\text{H}_2\text{O}$
6.70	31.27	13.92	38.82	
0.00	37.23	11.54	38.26	Solid solution
0.05	43.95	8.54	43.90	
0.04	43.50	13.43	45.40	
0.04	45.00	9.61	54.15	
0.27	48.40	8.60	50.60	
0.41	50.10	10.53	53.70	
0.04	74.50	6.54	73.10	

The study at 15°C. shows that the compounds formed are analogous to those formed at 18°C. and 25°C. In the basic region at 15°C. the solid solutions appear to be less basic than those formed at higher temperatures, but are otherwise entirely similar to those reported for other temperatures and require no discussion beyond that available in the literature. Basic compounds appear to be absent from the system at 15°C., since the point *E*, an experimentally determined value, represents, within the limits of error, a compound having the composition of the neutral salt. Point *A*, determined by the method of Baskerville and Cameron, represents the octadecyl hydrate of the neutral salt. In the acid region equilibrium was established very slowly, and consequently the data are less reliable. At 15°C. the concentration of acid which renders iron insoluble is lower than the concen-

TABLE 2

Composition of the solutions, the corresponding residues, and the solid phases in the system ferric oxide-sulfur trioxide-water at 15°C.

SOLUTION		RESIDUE		SOLID PHASES	TIE LINE LOCUS ^a
Fe ₂ O ₃	SO ₃	Fe ₂ O ₃	SO ₃		
<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>		
12.46	16.60	32.70	14.17	Solid solutions	None
14.61	21.23	20.30	11.86		
15.70	23.05	24.40	35.75		
16.70	22.38	56.50	12.28		
16.63	24.00	42.50	31.88		
17.61	26.45	19.80	28.70		
16.10	25.40	21.24	34.45	Fe ₂ O ₃ ·3SO ₃ ·18H ₂ O	A
15.86	24.98	18.26	28.20		
14.47	26.15	18.05	28.60		
14.20	28.25	15.23	29.12		
10.30	30.90	13.65	35.41	Fe ₂ O ₃ ·4.46SO ₃ ·19.2H ₂ O?	C
7.25	32.31	16.99	42.82		
2.48	35.23	11.58	41.47		
0.80	36.40	11.01	41.80		
0.01	37.20	9.33	39.40		
3.59	30.60	13.02	39.96	Fe ₂ O ₃ ·5.84SO ₃ ·30H ₂ O?	D
0.77	34.80	11.12	41.70		
0.01	37.20	9.33	39.40		
13.18	32.84	23.68	41.32	Fe ₂ O ₃ ·3.3SO ₃ ·10.3H ₂ O	B
10.04	33.21	21.55	40.05		
2.48	35.23	11.58	41.47		
0.80	36.40	11.01	41.80		
0.01	37.20	9.33	39.40		
7.02	29.39	14.99	42.33	Supersaturated for	D
0.98	30.32	8.84	42.89	Unsaturated for	D
18.81	32.98	59.13	35.08	An irregular value	
14.09	33.80	24.62	39.06	Supersaturated for	B
17.11	31.01	40.12	47.47	Supersaturated for	A
18.75	31.94	38.60	37.41	Supersaturated for	A
15.65	42.27	23.92	42.09	Supersaturated for	B
17.75	31.85	43.06	44.03	Supersaturated for	A

^a See figure 1 for the locations of these loci.

Analysis of the ferric sulfate: Fe₂O₃, 30.21 per cent; SO₃, 45.51 per cent.

trations necessary to produce insolubility at 18° and 25°C. In the present study the only rational formula indicated for the acid region is the one at point *D* in figure 1, and is approximately Fe₂O₃·6SO₃·30H₂O.

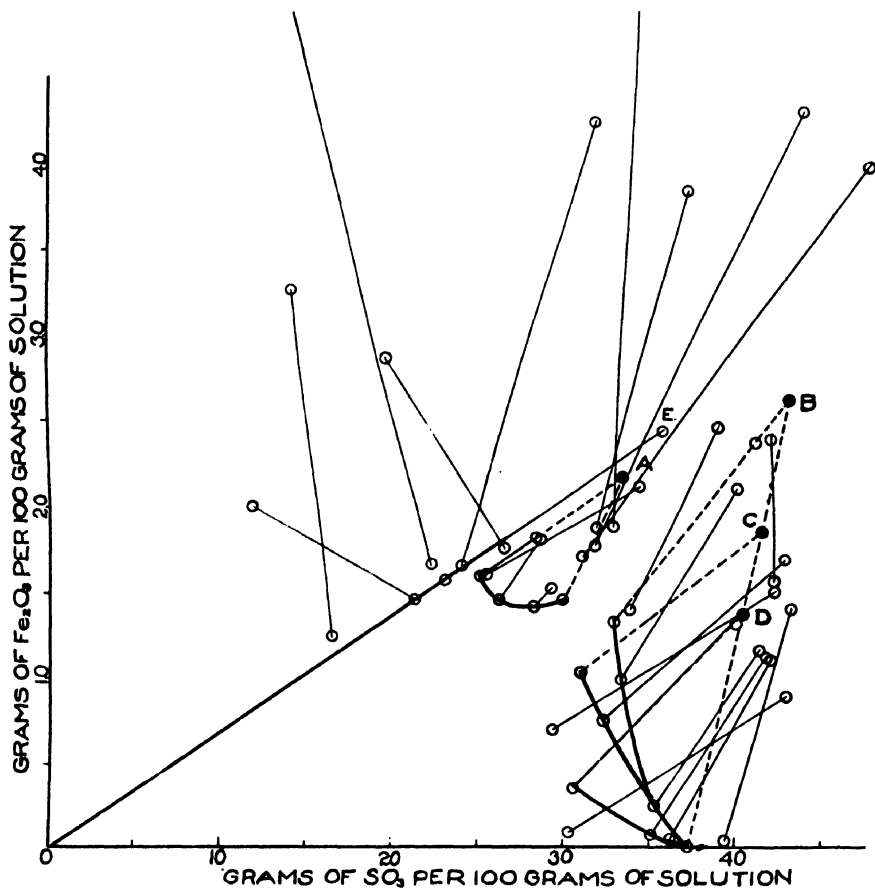


FIG. 1. Solubility curves, residues, tie lines, and solid phase in the system ferric oxide-sulfur trioxide-water at 15°C.

- | | |
|---|---|
| A, $\text{Fe}_2\text{O}_3 \cdot 3.0\text{SO}_3 \cdot 18.0\text{H}_2\text{O}$ | B, $\text{Fe}_2\text{O}_3 \cdot 3.3\text{SO}_3 \cdot 10.3\text{H}_2\text{O}$ |
| C, $\text{Fe}_2\text{O}_3 \cdot 4.46\text{SO}_3 \cdot 19.2\text{H}_2\text{O}$ | D, $\text{Fe}_2\text{O}_3 \cdot 5.84\text{SO}_3 \cdot 30.0\text{H}_2\text{O}$ |
| E, $\text{Fe}_2\text{O}_3 \cdot 2.93\text{SO}_3 \cdot 17.8\text{H}_2\text{O}$ | |

SUMMARY

At 10°C., in the system ferric oxide-sulfur trioxide-water, the ferric sulfate and sulfuric acid appear to form solid solutions rather than acid salts when the concentration of sulfur trioxide exceeds 37 per cent. At 15°C. the system does not appear to form basic salts.

In the neutral region the salt formed appears to be the octadecyl hydrate.

In the acid region the information is too meager to justify definite statements, but the existence of a salt of the composition $\text{Fe}_2\text{O}_3 \cdot 6\text{SO}_3 \cdot 30\text{H}_2\text{O}$ is indicated.

The compounds formed at 15°C. appear to be more highly hydrated than those formed at 18° and 25°C.

Iron becomes insoluble in a lower concentration of sulfuric acid at 15°C. than at 18° or 25°C.

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LODOCHNIKOV'S METHOD OF REPRESENTING POLYNARY SYSTEMS¹

MERLE RANDALL AND BRUCE LONGTIN

Department of Chemistry, University of California, Berkeley, California

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I. QUATERNARY SYSTEMS

A novel method of representing the phase relations in quaternary systems, using a two-dimensional diagram, has been described by Lodochnikov (1, 2, 3).^{2,3} The method possesses certain obvious advantages and other serious disadvantages. One of the principal disadvantages is the difficulty with which the meaning of the diagrams may be visualized. In this paper we shall attempt to simplify Lodochnikov's presentation by showing the geometrical relationships that exist between his diagrams and familiar projections of tetrahedral phase models. As far as possible we shall use conventions and symbols which parallel American usage.

Lodochnikov's method

Lodochnikov's method consists essentially in representing each composition (N_1, N_2, N_3, N_4) of a single phase by two points in a triangular diagram. He uses the equilateral right triangle (OAB in figure 1) of Roozeboom (5). On the vertical axis he plots the mole fraction, N_3 , of the component X_3 .

Along the horizontal line \overline{PR} at this height he lays off the distance \overline{PS} from the vertical axis, equal to the mole fraction, N_2 , of the component X_2 . From the point Q , in which the diagonal side of the triangle intersects \overline{PR} , he lays off the distance \overline{QT} in a negative direction, equal to the mole fraction, N_1 , of the component X_1 . Lodochnikov considers the line segment \overline{ST} as a *vector* by which he represents the composition of the phase.

Since $\overline{QR} = \overline{RA} = N_3$, and the distance $\overline{OA} = \overline{PR}$ is taken as unity, the distance \overline{ST} represents the mole fraction, N_4 , of the fourth component, X_4 , in the phase. The same property holds when the compositions are

¹ Clerical assistance of the Works Progress Administration of the United States Government is gratefully acknowledged. (OP-465-03-3-147)

² Reference 1 includes a lengthy review of methods of representing multicomponent systems.

³ Reference 3 describes construction for five-, six-, seven-, eight-, etc., component systems.

expressed in weight fractions (or in weight per cent if we take \overline{OA} equal to 100 per cent).

Since \overline{PT} is therefore equal to $(N_2 + N_4)$, the two points which he plots have the coördinates $(X = N_2, Y = N_3)$ and $(X' = N_2 + N_4, Y = N_3)$ respectively. The diagram may be obtained directly by plotting two points with these coördinates.

Lodochnikov also proposed the use of an equilateral triangle, as shown in figure 2, but prefers the right triangle. While there are a number of reasons why the right triangle should be preferred (in addition to less expense for paper), the authors feel that the equilateral triangle is too firmly established in American usage to be replaced.

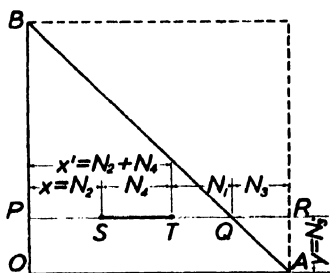


FIG. 1

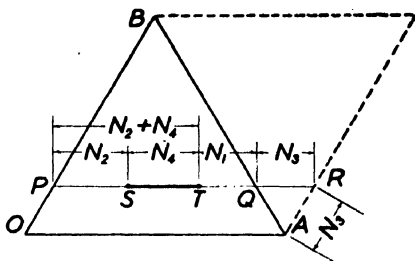


FIG. 2

FIG. 1. Lodochnikov's representation in Roozeboom's right triangle

FIG. 2. Lodochnikov's representation in Gibbs' equilateral triangle

Tetrahedral coördinates

It is customary to use a tetrahedral model or one of its projections in representing quarternary systems. Tetrahedral (as well as triangular) coördinates⁴ were first proposed by the astronomer Möbius (4) in his geometric studies of the center of gravity. He showed that if we place the masses X_1 , X_2 , X_3 , and X_4 at the vertices of a regular tetrahedron whose altitudes are unity, each of the perpendicular distances from the center of gravity to a face of the tetrahedron is equal to the ratio of the mass situated at the opposite vertex to the total masses. For instance in figure 3, if G is the center of gravity, then the perpendicular distance h_3 is equal to the ratio $X_3/(X_1 + X_2 + X_3 + X_4)$.

If we pass a plane through the center of gravity parallel to one of the faces of the tetrahedron, it cuts off equal intercepts on the three edges of the tetrahedron, which are proportional to the distance, h , between the center of gravity and the face. If we take the edges rather than the altitudes of the tetrahedron equal to unity, then these intercepts are equal to the particular mass ratio (e.g., to $X_3/(X_1 + X_2 + X_3 + X_4)$ in figure 3).

⁴ Gibbs was well acquainted with the work of Möbius (4) and undoubtedly derived his concept of triangular and tetrahedral coördinates from this source.

If the masses which we locate at the vertices of the tetrahedron are each equal to the number of moles of one component in a phase, then the mass ratios involved (e.g., $X_3/(X_1 + X_2 + X_3 + X_4)$) are the mole fractions of the various components. Depending on the choice of the unit length we represent the mole fractions either by the distance of a representative point from each of the faces of the tetrahedron (Gibbs), or by the distances through the point parallel to the faces of the tetrahedron (Roozeboom). If the masses X_1 , X_2 , X_3 , and X_4 are expressed in other than mole units we may represent weight fractions, weight per cents, or other composition units by these coördinates.

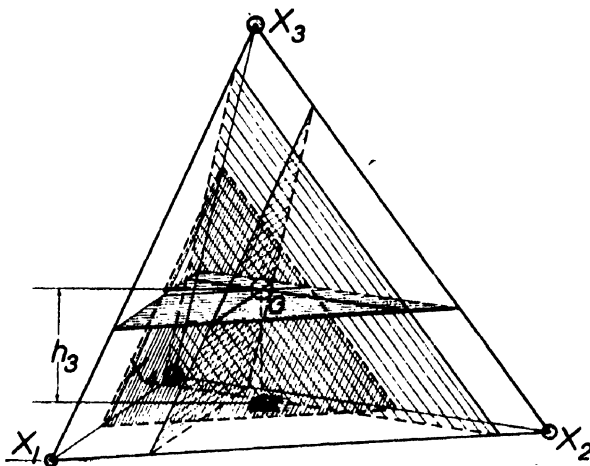


FIG. 3. Möbius' tetrahedral coördinates

Projections

In representing any solid model (e.g., $X_1X_2X_3X_4$ of figure 4) it is customary to use a plan and an elevation view. Actually it is only necessary to use any two independent projections.

Let us project the tetrahedral model by rays parallel to the edge $\overline{X_1X_4}$ (e.g., the ray $\overline{GG'}$ in figure 4). Since the edge $\overline{X_1X_4}$ lies in both the faces $X_1X_2X_4$ and $X_1X_3X_4$, each such ray is parallel to both of these faces. Hence the distance from any point on one of these rays (e.g., G''') to one of these two faces, measured parallel to one of the other edges (e.g., the distance $\overline{P'''G'''}$), is equal to the corresponding distance measured from G (e.g., \overline{PG}).

Let us use any plane parallel to $X_1X_2X_3$ as a projection plane. Then the face $X_1X_2X_3$ will project into an equilateral triangle $X'_1X'_2X'_3$ which is exactly congruent to the original triangle. Since the two vertices X_1 and X_4 lie on the same projection ray, the projected view of X_4 coincides with X'_1 , and the projected face $X_2X_3X_4$ coincides with $X'_1X'_2X'_3$. The two

faces $X_1X_3X_4$ and $X_1X_2X_4$ are seen edgewise, and appear as the straight lines $X'_1X'_3$ and $X'_1X'_2$, respectively.

The point G is projected as G' . In figure 4 the distance $\overline{P'G'}$ is measured parallel to $\overline{X'_1X'_2}$ and hence parallel to the edge $\overline{X_1X_2}$ of the tetrahedron. It is therefore equal to the mole fraction, N_2 , of the component X_2 in the phase represented by point G . The distance $\overline{P'X'_1}$ is similarly equal to the mole fraction, N_3 , of component X_3 in the phase represented by G . Hence in order to obtain this view by plotting from data, we merely consider the system as composed of the three components X_2 , X_3 , and a lumped component $(X_1 + X_4)$.

Similarly we may obtain a second view by projection onto any plane parallel to the same face, by rays parallel to the edge $\overline{X_2X_4}$. The view may be obtained from data by considering the system to consist of the three components X_1 , X_3 , and a lumped component $(X_2 + X_4)$. Of

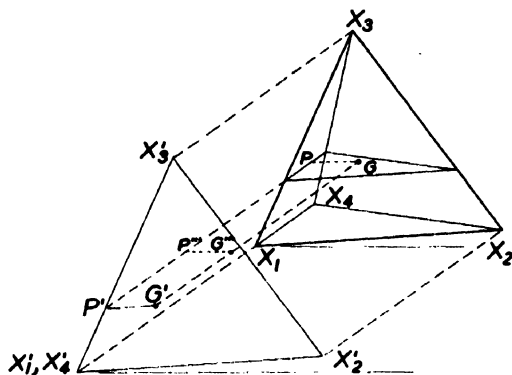


FIG. 4. Projection of Möbius' tetrahedron to obtain the left point of Lodochnikov's "vector"

course, it is important to place the component X_3 at the top vertex of the triangle in each view, component X_1 , whether alone or lumped with X_4 , at the left, and X_2 at the right. In the second view the point G appears as a point G'' whose triangular coordinates are N_3 measured upwards and N_1 measured from the right side leftwards.

The two views of the tetrahedron are shown in figure 5. They are the views we would obtain by looking at the tetrahedron from a great distance, first along the edge $\overline{X_1X_4}$, and then along $\overline{X_2X_4}$.⁵ Since the point G does not lie in the front face of the tetrahedron, there will be parallax, so that the point appears to shift from G' to G'' in going from one viewpoint to the other. The amount of this parallax is exactly proportional to the

⁵ Actually in looking at the tetrahedron in this way there will be a slight distortion so that the outline appears isosceles rather than equilateral. The parallel projection plane was used to avoid this distortion.

depth at which G lies behind the front face of the tetrahedron and is the length of Lodochnikov's "vector."

By comparison of these two views with figure 2 it is apparent that point G' is point S and G'' is T . Lodochnikov's representation may be obtained by superposing these two views. When Lodochnikov's method is of value, this superposition should be made, but ordinarily the superposition leads only to confusion. In any case it is better to keep in mind that his representation consists of two different views of a tetrahedron.

Use of the projections

In the tetrahedral model representing a particular system the important features are the equilibrium surfaces and their intersections, together with crystallization paths (i.e., intersections of planes with an equilibrium surface) and straight lines radiating from the point representing pure compounds. In the use of the model it is important to be able to locate

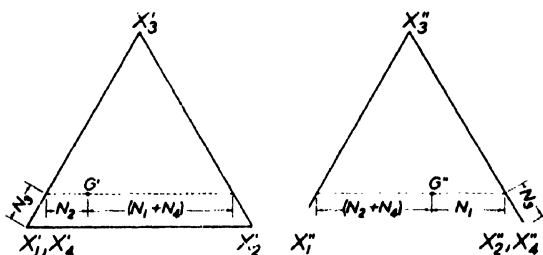


FIG. 5. Separated projections showing left and right ends of Lodochnikov's "vector"

intersections of straight lines with curved surfaces, with planes, and with other straight lines, and to pass a straight line through a given point.⁶ In the projected views these problems become familiar problems in projective geometry, whose solutions may be found in any of a large number of texts on that subject. For this reason as well as others it is important to keep the two views of the tetrahedron in mind as separate projections.

Representation of a surface

In representing a surface projectively it is customary to draw some form of contour lines on the surface and represent them in the projection. In figures 6 and 7 we have illustrated the representation of a particular surface *ram* by three different means, using contour lines. Since the curve *ma* lies in the front face of the tetrahedron, it shows no parallax in the two views (figure 7), and hence in the superposed view of Lodochnikov (figure

⁶ Lodochnikov demonstrated the methods of solving these problems on his diagram with some difficulty because he was "not well acquainted with the principles of projective geometry which were involved."

6b) appears as a single curve. None of the radial contours lies in the front face; hence each of them shows parallax and appears in Lodochnikov's view as two different curves which intersect on the curve ma (the only point on the contour which lies in the front face and shows no parallax is this intersection). The curve pq , which lies in a plane *parallel* to the front face, shows parallax, but no change in shape.

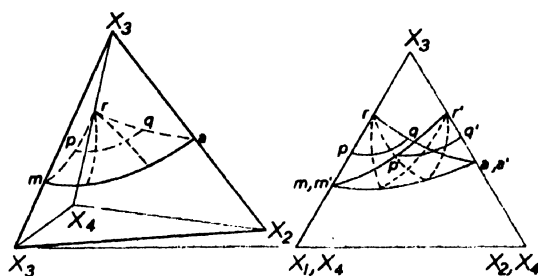


FIG. 6. Representation of a surface in a regular tetrahedron by (a) cabinet projection and (b) Lodochnikov's simultaneous projection.

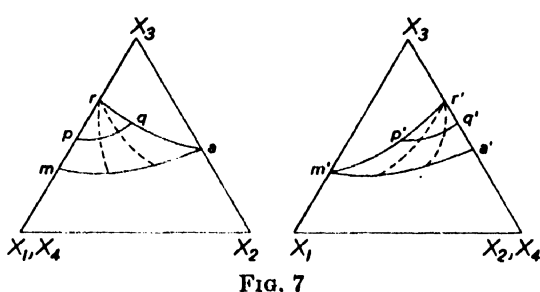


FIG. 7

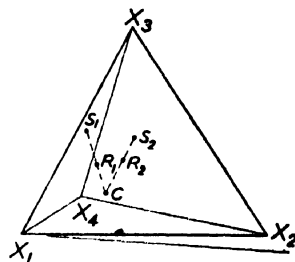


FIG. 8

FIG. 7. Representation of a surface in a regular tetrahedron by two separate projections

FIG. 8. Schreinemakers' method of residues

Center of gravity property

It is apparent from Möbius' derivation that two phases of different total amounts and compositions are represented by the centers of gravity of two different distributions of masses at the vertices of the tetrahedron. Furthermore, if we combine these two phases into a single phase, the combined phase is represented by the center of gravity of the combined masses.

It is an elementary principle of physics that the center of gravity of two or several distributed masses may be found by concentrating each of the distributed masses at its center of gravity and then locating the center of gravity of these concentrated masses. Hence we may represent both the composition and total amount of a phase by endowing the representative

center of gravity in tetrahedral coordinates with a mass equal to the total amount of material present in the phase. When two phases are combined in any proportions, the two samples being combined are represented by two such mass points, and the combined phase by the total mass concentrated at their center of gravity. This property, which is quite well known, is useful in the graphical solution of material balance problems.

Schreinemakers' method of residues (6)

From two different solutions S_1 and S_2 (figure 8) we have obtained supposedly the same solid phase, C . In analyzing the product we may determine the compositions of the solutions accurately, but we can only obtain analyses for the composition of the solid, C , on residues R_1 and R_2 to which some of the solution adheres. Since R_1 is a combination of some of the solid phase C with some of the solution S_1 , it is a center of gravity

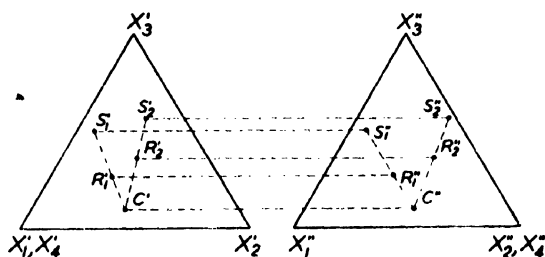


FIG. 9

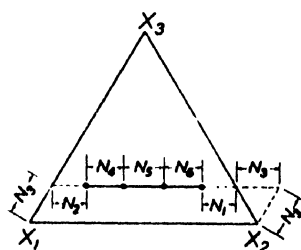


FIG. 10

FIG. 9. Schreinemakers' method of residues adapted to two-projection representation

FIG. 10. A representation of a six-component system

of the two points S_1 and C . Similarly, R_2 is the center of gravity of S_2 and C . Since the center of gravity of two mass points lies on the straight line joining them, point C must lie at the intersection of two straight lines, one through S_1 and R_1 , and the other through S_2 and R_2 .

In our projections (figure 9) the location of the point C representing the unknown composition of the solid phase is a simple problem in projective geometry,—that of finding the intersection of two straight lines. In both views C will appear as the intersection of the lines $\overline{S_1R_1}$ and $\overline{S_2R_2}$. It is important to note that in both views each single point must appear at the same height, since the projection rays are both parallel to the base of the tetrahedron. If the two lines do not actually intersect in the solid model, there will be parallax between them, and the apparent intersection will shift vertically as well as horizontally in the two views. Such a behavior indicates either errors in analyzing or plotting the compositions, or that the solid phases were not actually the same in the two cases.

Other applications of the center of gravity property lead to other

problems in projective geometry which are as readily solved as the two examples we have given. We intend to discuss some of these more in detail in subsequent papers.

II. POLYNARY SYSTEMS

It is possible to represent completely the composition of a *single* phase containing any number of components by means of triangular coördinates. This is accomplished by lumping the components in three groups and considering each group of components as a single lumped component. One such grouping will give a single point. We need a number of points to represent an m -dimensional model in two dimensions. Hence we shall need to regroup the components in a sufficiently large number of independent ways in order to represent completely the composition of the phase.

One such method is shown in figure 10. The three components X_1 , X_2 , and X_3 are always represented at the three corners of the triangle. For the first projection all of the remaining components are grouped with X_1 , so that the principal coördinates are N_2 and N_3 . Then we move component X_4 , grouping it with X_2 . The principle coördinates are now N_3 and $(N_2 + N_4)$. The point has shifted to the right a distance equal to the mole fraction, N_4 , of the component which was shifted. We continue shifting components from the left to the right vertex of the triangle, and with each shift the representative point moves to the right an amount equal to the mole fraction of the component which was shifted. The mole fraction of each component may be read directly from the diagram by reading the distances between successive points.

It may be proved that in order to represent completely any m -dimensional model in n -dimensional space only (m/n) projected views are necessary. We have used four points in figure 10 to represent a point in a five-dimensional model, where we only needed $5/2$ or two and one-half (i.e., three) points. Lodochnikov found a method of grouping the components which required a minimum number of points. The method which we present below is only a slight modification of his method.

Let us start with all of the components beyond X_3 grouped with X_1 . Then each time we regroup one even-numbered component with X_2 ; we will simultaneously regroup an odd-numbered component with X_3 . When we shift component X_4 over to the X_2 corner, we must simultaneously shift component X_5 over to the X_3 corner. The representative point moves parallel to the side $\overline{X_1X_2}$ a distance equal to the mole fraction N_4 , and simultaneously a distance parallel to $\overline{X_1X_3}$ equal to the mole fraction N_5 .

In this way the composition of a single phase is completely represented by a broken line. This broken line may be considered as made up of a

number of vectors. The component of each vector parallel to $\overline{X_1X_2}$ represents the mole fraction of one of the even-numbered components of the phase, while the component parallel to $\overline{X_1X_3}$ represents the mole fraction of one of the odd-numbered components of the phase. The broken line always starts at the vertex, X_1 , of the triangle. It may be shown that, in order for the mole fractions to total unity, it must end on the side opposite this vertex (i.e., $\overline{X_2X_3}$).

Problems involving the center of gravity property, such as Schreinemakers' method of residues, may be readily solved in this projection (figure 12). It is only necessary to recognize that the different points on a single broken line are different views of a single point in the m -dimensional model. The different views of the two lines $\overline{S_1R_1}$ and $\overline{S_2R_2}$ must each show them intersecting in a point which is one of the views of the point C .

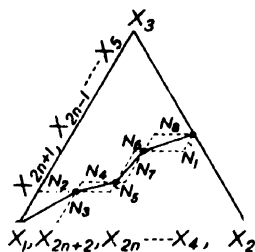


FIG. 11

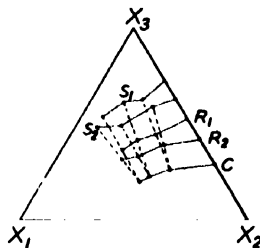


FIG. 12

FIG. 11. An eight-component phase in a multicomponent system by a modification of Lodochnikov's representation

FIG. 12. Schreinemakers' method of residues in an eight-component system

A false solution of the problem is to be detected by the ratio in which the lines $\overline{S_1R_1C}$ and $\overline{S_2R_2C}$ are divided by the point C in each view. If C is a true intersection, the ratio will be the same in all views. If not, this ratio will change.

This method of representing polynary systems offers no particular advantages in representing regions of more than two or at the most three degrees of freedom. It does permit us to represent completely any region in m dimensions which has no more than three degrees of freedom. However, in representing such regions by this method it becomes necessary to separate the different views of the m -dimensional model in order to avoid confusion.

SUMMARY

We have shown that Lodochnikov's method of representing systems is equivalent to two simultaneous projections upon one face of a tetrahedron. We have also simplified Lodochnikov's order of plotting to conform to

American usage of always plotting towards the position representing the pure component. In the solution of phase problems we have found it desirable to place each of the two or more simultaneous projections in separate triangles. We have also indicated the solution of a simple problem in polynary systems by the use of an extension of the projective principles which we have presented.

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THE VISCOSITY OF SOLS MADE FROM X-IRRADIATED APPLE PECTIN

C. H. DWIGHT AND H. KERSTEN

Department of Physics, University of Cincinnati, Cincinnati, Ohio

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INTRODUCTION

In a previous paper (2) the authors described experiments upon the viscosity of sols which had been made from x-irradiated agar. It was concluded (i) that irradiation of dry agar by soft x-rays decreases the viscosity of the resulting sol, (ii) that there is no appreciable "recovery" of the dry agar from the effects of irradiation, at least within seventeen days, (iii) that the effect on the agar is not due to heat emanating from the target of the x-ray tube, and (iv) that irradiation of the dry agar slightly decreases the pH of the resulting sol. The present paper covers experiments upon apple pectin, with a view towards (i) the finding of an effect similar to that observed in the case of agar, when the sol is made up of an irradiated sample, (ii) the extension of the "recovery time," and (iii) showing that pH plays probably only a minor part in the experiments.

EXPERIMENTAL

As in the previous experiments, the x-rays were supplied by a copper target gas x-ray tube (1) operated at 37 peak kilovolts and 10 milliamperes. The window of the x-ray tube was made of thin aluminum and Cellophane, so that the most intense part of the radiation passing through it had a wave-length of 1.54 Å. Powdered apple pectin was irradiated in the cavity of a drop-culture slide, placed about 3 cm. from the focal spot of the x-ray tube. Each sample was irradiated for 3 hr., and, after having been irradiated, was mixed, and divided into several parts, each containing 0.12 g. These portions of the original sample were placed in flasks to which 20 cc. of buffer solution was added. pH concentrations from 1.76 to 6.95 were used. Control samples were made in exactly the same way, except that unirradiated pectin was used. In any one experiment three parts of a given sample, in buffers of as many different pH values, together with three controls, were employed.

In order to insure uniformity in the diffusion of the powder within the liquid, the six flasks were placed in a rocking frame operated by an electric motor. The flasks, frame, and motor were placed in an electrically heated

oven, the temperature of which was kept at about 70°C. by a thermoregulator. A decrease in the density of the sol, due to evaporation while being heated, was prevented by closing the tops of the flasks with rubber caps. After agitation for 30 min. the motion was stopped, and the heater turned off. The flasks were then allowed to cool for 2 hr., in which time the sols were assumed to have reached room temperature and have "zero age."

A definite amount of each sol was pipetted into six separate Ostwald viscosity pipets, which were so arranged that suction or pressure could be

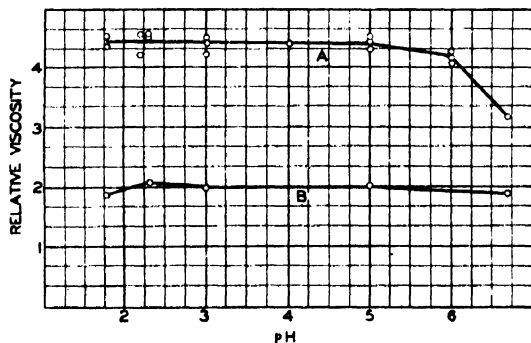


FIG. 1. Plot of relative viscosity of sol against pH. A, controls; B, irradiated powders. Sols of same age.

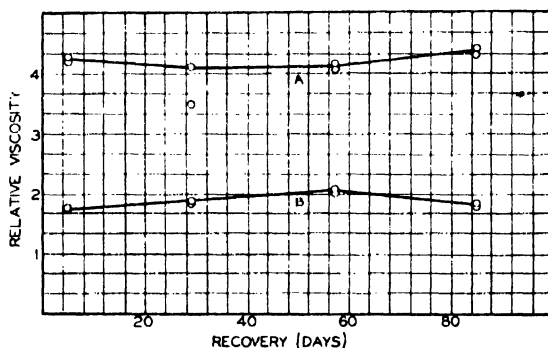


FIG. 2. Plot of relative viscosity against time for "recovery" of the pectin from the effects of irradiation. A, controls; B, irradiated powders. pH = 5.

applied singly or collectively to them by connecting the top "bus" tube to a small rotary pump or to the laboratory air compressor, respectively. Much greater convenience and dispatch were thus effected. After the experiment the viscosity pipets could be washed and dried simultaneously. The time of flow of the sol through the viscosimeters was observed with a stopwatch, and divided by the time of flow of distilled water at approximately the same temperature through the same viscosimeter. This quotient was taken as the "relative viscosity" of the particular sol. Check

readings were taken to show that within the time of the experiment there was little or no "age" effect in the sol.

The results obtained from these experiments are plotted in figure 1, which shows (i) that there is a marked difference between the controls (A) and the irradiated samples (B), (ii) that the effect of pH variation is unimportant, at least in comparison with (i), and (iii) that there is little effect due to the "age" of the sol, shown by the closeness of the points plotted at given pH values, throughout the time required for the experiment.

In order to investigate the possible "recovery" of the apple pectin powder from the effects of irradiation, a relatively large amount of the pectin was irradiated and then set aside in a bottle identical with that which contained the control. At the end of five days a sample (0.12 g., as previously) was run through a viscosity pipet, and the relative viscosity determined. A control was also run. This procedure was repeated at the end of twenty-nine, fifty-seven, and eighty-five days. In each case a pH of 5.0 was used for the sol. Figure 2 indicates that there is little recovery of the powder even after two and a half months.

CONCLUSIONS

1. As was the case with agar, irradiation of dry apple pectin powder by soft x-rays profoundly affects the viscosity of the resulting sol.
2. The effect of pH variation is not very important in comparison with the effects due to irradiation.
3. There is no appreciable recovery of the dry pectin powder from the irradiation, even after eighty-five days.

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THE DIELECTRIC ABSORPTION AND DIELECTRIC CONSTANT OF SOLUTIONS OF ALIPHATIC AMINO ACIDS

HUGO FRICKE AND ADOLF PARTS

Walter B. James Laboratory for Biophysics, The Biological Laboratory, Cold Spring Harbor, Long Island, New York

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Linhart (15) has reported a region of anomalous dispersion in solutions of glycine and certain other amino acids at wave lengths around 1 meter. The principal subject of this paper is a study of the dielectric absorption of solutions of some of the aliphatic amino acids on the long wave length side of this region. In the range of wave lengths used the dielectric constant is still practically constant. The values of dielectric absorption obtained by us are considerably smaller than would be expected from Linhart's measurements, and his conclusion that the relaxation time is that of a structure many times greater than the amino acid molecule is not confirmed by our work.

EXPERIMENTAL PROCEDURE

The method consists in balancing, in a resonance circuit, two identical microelectrolytic cells, one of which contains the amino acid solution and the other a solution of potassium chloride. The cells are balanced by changing the concentration of potassium chloride and by varying a parallel condenser. The experimental arrangement is shown in figure 1. The apparatus contains two interchangeable push-pull valve generators, G, one of which can be operated between 2.05 and 16.4 megacycles, and the other between 16.4 and 65.6 megacycles. The resonance circuit A contains the interchangeable inductance L, the variable condenser C, the micro condenser C_i and the electrolytic cell E. The electrolytic cell is inserted into the circuit at P_1 and P_2 by banana plugs and jacks. Part of the resonance circuit is surrounded by the tight grounded copper shield S, but C_i and E are placed outside the shield in order to make these units easily accessible. The axis of C is extended with a hard rubber rod which passes through the shield so that it is possible to vary C without opening the shield.

C_i contains two plates, 2.5 cm. in diameter. The capacity is varied by varying the distance between the plates, for which purpose one of the plates is mounted on a micrometer screw. In the position where C_i is usually used, its capacity can be read to an accuracy of $0.001 \mu\mu f$.

A is tuned to resonance by varying C_t , which is actuated at a distance by a pulley and thread arrangement. The point of resonance and the intensity of the oscillating current are recorded by the tube voltmeter T.

By an arrangement not shown in figure 1, the cell and the microcondenser C_t can be introduced into one arm of a resistance-capacity bridge, allowing measurements to be made between 0.25 and 2048 kilocycles.

The generators were calibrated by means of a cathode ray oscillograph. An auxiliary oscillator was adjusted to a frequency of 2.05 megacycles by means of a wavemeter. Through an inductive coupling, this oscillator impressed an oscillating potential on one of the pairs of plates of the oscillograph, while the other pair of plates was connected to the resonance circuit at P_1 and P_2 . With the resonance circuit kept tuned, frequencies of 2.05,

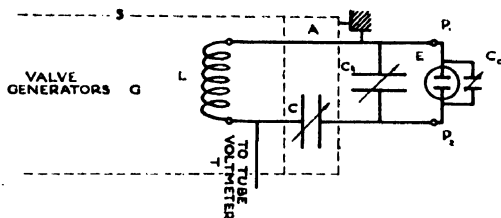


FIG. 1

FIG. 1. Diagram of resonance apparatus

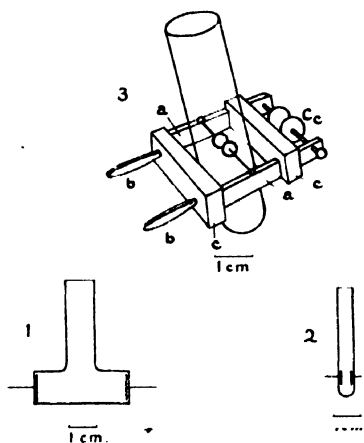


FIG. 2

FIG. 2. Electrolytic cells

4.10, 8.19, and 16.4 megacycles were now established on one of the generators by the well-known method of producing certain types of stationary patterns on the oscillograph. This generator was thereafter used (at 16.4 megacycles) instead of the 2.05-megacycle oscillator for calibrating the other generator, which was used at 16.4, 32.8, and 65.6 megacycles.

The construction and mounting of the cells (No. 3) chiefly used in the present work are shown in figure 2. The cell has the form of a test tube 1.4 cm. in diameter. The electrodes are of platinum, 4.5 mm. in diameter and approximately 4 mm. apart. Connection through the glass is made by platinum wire 0.75 mm. in diameter and 6 mm. long. These wires connect to the brass rods (a) which carry the banana plugs (b). The whole unit is kept rigid by means of two narrow strips of Vicron (c). This material has excellent dielectric properties, and tests showed that the presence of the strips introduced no appreciable damping in the circuit.

A small condenser, C_c , is placed across the cell, rigidly attached to the cell mounting. This condenser consists of a stationary plate and a movable plate, mounted on a small micrometer screw. The plates are 8 mm. in diameter, and the leads are 3 mm. in diameter. The condenser cannot be read directly with sufficient accuracy, but each time it is reset the change in its capacity is recorded by measurement at low frequency.

At the frequencies and conductances used in the present work, the influence of electrode polarization is negligible, even when blank electrodes are used. However, the electrodes of the cells were platinized in order to make it possible to use them at low frequencies also.

For the purpose of control, certain of the measurements were also made with two other types of cell (cells No. 1 and No. 2), shown in figure 2. The dimensions of these cells will be clear from the figure.

The measurements were made in a room kept at a constant temperature, which was 21.0°C. when not otherwise indicated.

In order to make a measurement on an amino acid solution the procedure is as follows: The condenser, C_c , on the cell with the potassium chloride solution, referred to as the K cell, is adjusted so that the capacities of the filled cells are nearly alike. C_c on the cell containing the amino acid solution (the A cell) is set at zero. The A cell is placed in the resonance circuit and the reading on the galvanometer of the tube voltmeter, at resonance, is recorded. The condition of resonance is established by varying C_t . The A cell is now replaced by the K cell, and the concentration of potassium chloride is changed until the reading on the tube voltmeter at resonance is the same as before. The low-frequency conductance of the potassium chloride solution is thereafter measured with the bridge. At the same time, the low-frequency conductance of the amino acid solution is also recorded, to make it possible to correct for slight changes in the conductance of this solution, caused by temperature fluctuation, etc. In actual practice the potassium chloride is adjusted twice, to give readings on the tube voltmeter which are slightly lower and slightly higher than the readings obtained for the amino acid solution. The low-frequency conductance of each of these two potassium chloride solutions is recorded, and by interpolation the low-frequency conductance of the potassium chloride solution which exactly balances the amino acid solution is obtained.

The difference in settings on C_t , with the amino acid solution and the potassium chloride solution, respectively, in the circuit, must not exceed a certain value, known from preliminary measurements. If the difference is too high, C_c is reset and the comparison repeated. In the range of frequencies used, the dielectric constant of the amino acid solution changes so little with frequency that we can use the same setting of C_c at all the different frequencies.

A typical resonance curve, *viz.*, readings on the tube voltmeter against

readings on C_t obtained at 65.6 megacycles, is shown in figure 3. The curve was obtained at a conductance of $33 \times 10^{-8} \text{ ohm}^{-1}$. The resonance curves are perfectly symmetrical, showing that there is no appreciable interference of the resonance circuit with the generating circuit.

The dielectric constant $\epsilon_a(\omega)$ and the conductivity $\kappa_a(\omega)$ of the amino acid solution are obtained from the equations:

$$\frac{10}{36\pi} \times \frac{\epsilon_a(\omega)}{k} = \Delta C + \frac{10}{36\pi} \times \frac{\epsilon_o(\omega)}{k} \quad (1)$$

$$\kappa_a(\omega) = \kappa_o(\omega) \quad (2)$$

$\epsilon_o(\omega)$ and $\kappa_o(\omega)$ are the dielectric constant and conductivity, respectively, of the potassium chloride solution at the frequency ω ; k is the cell constant, defined on the basis of electric conductance measurements; ΔC is the differ-

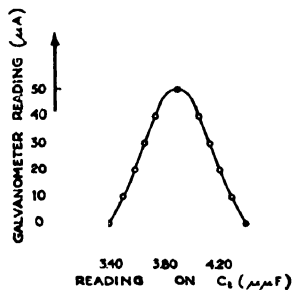


FIG. 3



FIG. 4

FIG. 3. Resonance curve

FIG. 4. Diagrammatical representation of cell assemblage

ence in condenser readings (in $\mu\mu\text{f}$) when the K cell and the A cell are in the circuit.

Under the experimental conditions used, the dielectric constant of the potassium chloride solution can be taken as equal to that of water.

The electric conductance of the potassium chloride solution is derived from the ionic conduction and from the dielectric absorption of the solvent. At the concentrations used, the ionic conductance can be taken as independent of the frequency. We can therefore write

$$\kappa_o(\omega) = \kappa_o(o) + \kappa_o^d$$

where κ_o^d is the specific electric conductance of water due to its dielectric absorption. $\kappa_o(o)$ is the low-frequency specific electric conductance of the potassium chloride solution, obtained directly in the measurement. We introduce

$$\kappa_a^d = \kappa_a(\omega) - \kappa_a(o)$$

as the difference between the specific electric conductance of the amino acid solution at high and at low frequency, and we obtain:

$$\kappa_a^d - \kappa_o^d = \kappa_o(o) - \kappa_a(o) \quad (3)$$

DISCUSSION OF METHOD

The validity of equations 1 and 2 is based on the following assumptions: (1) The consumption of electric energy at the surface of the electrodes (electrode polarization) is negligible. (2) The inductance of the cell assembly can be neglected. (3) Electric energy flows to and from the fluid by way of the stray capacities which connect the different elements of area of the enveloping surface of the fluid with each other and with the leads to the cell. This flow of energy can be neglected in the comparison of the two cells.

That these requirements are met to a sufficient extent under the experimental conditions used is shown by various kinds of control measurements described below.

The influence of the stray capacities is comparatively small because of the high dielectric constant of the fluids investigated. The following considerations are presented for the purpose of elucidating the influence of this source of error. Although the cell assembly cannot be strictly represented by any simple network of conductances and capacities (inductance being neglected), for the present purpose we can use the representation shown in figure 4. In this diagram (C , σ) represents the admittance elements which solely involve the fluid.

$$C = \frac{10}{36\pi} \times \frac{\epsilon}{k}$$

$$\sigma = \frac{\kappa}{k}$$

C_1 represents the admittance elements (capacities between the leads to the cell) which solely involve the dielectric (mainly air) surrounding the fluid and ($C_m C_i \sigma_i$) represents the admittance elements which involve partly the fluid and partly the dielectric. C_m is independent of the fluid and we can write

$$\sigma_i = \frac{\kappa}{k'}$$

$$C_i = \frac{10}{36\pi} \times \frac{\epsilon}{k'}$$

where k' is a constant dependent on the geometry of the cell assemblage. If we represent the complex admittance of the network ($C_m C_i \sigma_i$) by

$$1/z = \sigma' + jC'\omega \cdot 10^{-12}$$

then we obtain

$$\begin{aligned}\sigma' &= \frac{\sigma_i(1 + \alpha^2 \omega^2) \left(\frac{C_y a}{\sigma_i(1 + \alpha^2 \omega^2)} \right)^2}{1 + \left(\frac{C_y \omega}{\sigma_i(1 + \alpha^2 \omega^2)} \right)^2} \\ C' &= \frac{C_y}{1 + \left(\frac{C_y \omega}{\sigma_i(1 + \alpha^2 \omega^2)} \right)^2} \\ \alpha &= \frac{C_i}{\sigma_i} = \frac{10\epsilon}{36\pi\kappa} \times 10^{-12} \\ C_y &= \frac{1 + \alpha^2 \omega^2}{\alpha^2 \omega^2} \times C_i C_i \times 10^{-12} \\ &\quad \frac{1}{\alpha^2 \omega^2} (C_i + C_m)\end{aligned}$$

When the frequency is so high that

$$(\alpha\omega)^2 = \left(\frac{10\epsilon}{36\pi\kappa} 10^{-12} \omega \right)^2 \gg 1$$

we obtain

$$\begin{aligned}\sigma' &= \sigma_i \left(\frac{C_m}{C_i + C_m} \right)^2 \\ C' &= \frac{C_m C_i}{C_m + C_i}\end{aligned}$$

Because of the influence of ($C_m C_i \sigma_i$), the values of the specific electric conductance and the dielectric constant of the amino acid solution calculated from equations 1 and 2 are too high by the amounts $\Delta\kappa_a$ and $\Delta\epsilon_a$, respectively:

$$\begin{aligned}\Delta\kappa_a &= (\sigma'_{i-\epsilon_a} - \sigma'_{i-\epsilon_0})k \\ \Delta\epsilon_a &= (C'_{i-\epsilon_a} - C'_{i-\epsilon_0}) \times \frac{36\pi}{10} k\end{aligned}$$

$\Delta\kappa_a$ and $\Delta\epsilon_a$ are zero when the frequency is so low (or the electric conductance of the fluid so high) that

$$\left(\frac{10}{36\pi} \times \frac{\epsilon_0}{\kappa} \times 10^{-12} \omega \right)^2 \ll 1$$

and

$$\left(\frac{C_m \omega 10^{-12}}{\kappa} \times k' \right)^2 \ll 1$$

$\Delta\kappa_a$ and $\Delta\epsilon_a$ reach their highest values when the frequency is so high that

$$\left(\frac{10}{36\pi} \times \frac{\epsilon_o}{\kappa} \times 10^{-12} \omega \right)^2 \gg 1$$

This is the condition in our measurements. In this case and restricting ourselves to the case that

is smaller than, or of the order of, unity, we can write with sufficient accuracy

$$\begin{aligned} \frac{\Delta\epsilon_a}{\epsilon_a - \epsilon_o} &= \frac{k}{k'} \times \left(\frac{C_m}{C_m + \frac{10}{36\pi} \frac{\epsilon_a}{k'}} \right)^2 \\ \frac{\Delta\kappa_a}{\kappa_a} &= \frac{10}{36\pi} \times \frac{k}{(k')^2} \times \left(\frac{2C_m^2}{C_m + \frac{10}{36\pi} \times \frac{\epsilon_a}{k'}} \right)^3 (\epsilon_a - \epsilon_o) \\ &= \frac{2\Delta\epsilon_a}{\epsilon_a - \epsilon_o} \times \frac{\frac{10}{36\pi} \times \frac{\epsilon_a - \epsilon_o}{k'}}{C_m + \frac{10}{36\pi} \times \frac{\epsilon_a}{k'}} < \frac{2\Delta\epsilon_a}{\epsilon_a} \end{aligned}$$

Calibration measurements on cell No. 3 with fluids of known dielectric constant show that $\Delta\epsilon_a/\epsilon_a$ for the amino acid solutions studied is smaller than 0.5 per cent. Consequently the error introduced in our high-frequency conductance measurements with these cells, owing to the stray capacity of the cells, should not exceed 1 per cent.

CALIBRATION MEASUREMENTS

The value of k was determined by measuring the electric conductance of the cell at low frequency with solutions of potassium chloride of known concentration. The values of k for the cells used are given in table 3 (below).

These values were checked by measuring the capacity of the cell with fluids of known dielectric constant. These measurements serve essentially as a check on the error arising from the stray capacity. Alcohol, water, and mixtures of water and alcohol were used. The measurements were

carried out with a capacity bridge at 0.5 and 2 megacycles. The cell was filled successively with the different fluids, and for each fluid the bridge was balanced by varying a condenser in parallel with the cell. Taking the dielectric constant (ϵ_o) of water as a standard of reference, the dielectric constant ($\epsilon_{obs.}$) of any other fluid is obtained from

$$\epsilon_{obs.} = \epsilon_o - \frac{36\pi k}{10} \times C$$

where C (μmf) is the difference in readings on the parallel condenser. The results of these measurements for cells No. 2 and No. 3 are shown in table 1. The dielectric constants of water, alcohol, and their mixtures were measured by Wyman (20) at frequencies between 21.5 and 41.0 megacycles, and by Åkerlöf (1) at a frequency of 2 megacycles. The results of these two investi-

TABLE 1

Calibration of cells No. 3 and No. 2 by dielectric constant measurements on mixtures of water and alcohol

PER CENT ETHYL ALCOHOL (BY WEIGHT)	ϵ^*	$\epsilon_{obs.}$	
		Cell No. 3	Cell No. 2
0	80.3		
10.3	74.4	74.4	73.9
26.2	64.9	65.0	63.6
67.0	41.8	39.7	37.3
99.7	25.1	22.1	19.2

* References 1 and 20.

gators, which agree to within an accuracy better than 0.5 per cent, were averaged and the values are given in table 1. For the two mixtures of highest dielectric constant, the agreement between these values and those obtained by us with cell No. 3 is within the experimental error. For the fluids of lower dielectric constants our values are too low, as would be expected, owing to the influence of the stray capacities. Since the dielectric constant of the amino acid solutions is greater than that of water, in measuring these solutions the influence of the stray capacity would be smaller than it is in the case of the water-alcohol mixtures.

It is important to note, with respect to the significance of these calibration measurements, that the electric conductance of all the calibrating fluids is sufficiently low so that the current transported through the cell by conductance is negligible at the frequencies used. The value of the power factor at 2 megacycles lies between 0.02 and 0.04.

Before any pair of cells was used, it was ascertained that the cells showed no difference when compared with potassium chloride solutions in both, at

the different frequencies. This test was made with different concentrations of potassium chloride covering the range of electric conductance used in the work.

The effect on the measurements of transferring capacity from C_0 to C_t was determined in a preliminary study. It is of interest to note, as bearing on the permissibility of using an external condenser, that a nearly inappreciable error would have been introduced in our conductance values for the amino acids if C_t had been used exclusively instead of C_0 . The necessity for using C_0 instead of C_t is chiefly to avoid errors in the dielectric constants.

EXPERIMENTAL RESULTS

The following amino acids were studied: glycine, *dl*-alanine, *dl*- α -aminobutyric acid, *dl*- α -aminocaproic acid, γ -aminobutyric acid, and ϵ -aminocaproic acid. The materials were obtained commercially, and most of them were purified by one or more recrystallizations from water-alcohol mixtures. The recrystallization caused a marked decrease in the conductance of the solutions, but no change could be seen in the values of ϵ_a and κ_a^d .

The electric conductance of these amino acid solutions remains constant, to within our experimental accuracy, for frequencies below 16 megacycles. At higher frequencies the conductance increases, the values of $\kappa_a^d - \kappa_o^d$ varying as the square of the frequency within the range of frequencies tested. No change in the dielectric constant with frequency could be established with certainty. For ϵ -aminocaproic acid a slight decrease was found at the highest frequency, but it was just at the limit of the experimental accuracy. The results of our measurements are shown in table 2. Several of the solutions were measured with cells No. 1 and No. 2, as well as with cell No. 3. The values of $(\epsilon_a - \epsilon_o)$ obtained with cells No. 1 and No. 2 are generally slightly higher than those obtained with cell No. 3, as would be expected, owing to the influence of the stray capacities. As regards the values of $(\kappa_a^d - \kappa_o^d)$, no difference between the cells could be seen. In table 3 are shown the results obtained with these cells for 1 molar glycine.

Hedestrand (13) found that the dielectric constant of solutions of glycine and alanine varies linearly with the molar concentration over a wide range of concentrations. For glycine this linear relation was established up to 2.5*M*. This result was confirmed later by Wyman and McMeekin (22). The present measurements show that the relationship is not strictly linear, but there is a slight decrease in slope with increasing concentration. The deviation from linearity seems to be somewhat more strongly pronounced in the longer chain molecules.

In comparing our values for $\frac{\epsilon_a - \epsilon_o}{C}$ with those obtained by earlier investigators (2, 7, 8, 10, 11, 12, 13, 15, 22)* there is an uncertainty, owing to the

difference in temperature used. If we assume that $\frac{\epsilon_a - \epsilon_o}{C}$ decreases 0.25 per cent for each degree Centigrade increase in temperature (22), then our

TABLE 2
Dielectric measurements on amino acids

AMINO ACID	MOLES PER LITER (C)	$(\epsilon_a - \epsilon_o)/C$	$\kappa_a^d - \kappa_o^d / C$			VISCOSITY (RELATIVE) η/η_0	MOLAL VOLUME		
							Φ_1^*	Φ_d	Φ_o
Glycine.....	1.00	23.8	20.8	4.9	1.2	1.154	57.0	32.8	22.5
	2.00	23.6	24.5	6.0	1.5	1.362			
	2.70	23.4	26.1						
	3.00		27.4	6.7	1.6				
dl-Alanine.....	0.255	24.3	30.2			1.060	73.3	47.5	24.9
	0.941	23.9	33.8	8.7	2.8	1.286			
dl- α -Aminobutyric acid.....	0.332	25.0	39.3			1.104	89.6	56.6	
	0.927	24.3	46.5	10.9	3.3	1.401			
dl- α -Aminocaproic acid.....	0.077	24.1	60.0	15.0		1.05	122.2	84.0	
γ -Aminobutyric acid.....	0.202		85.0			1.072	89.6	70.3	
	0.927	50.3	114.0	28.0	6.4	1.44			
ϵ -Aminocaproic acid.....	0.196	86.8	234.0			1.110	122.2	118.0	
	0.775	86.5	326.0	82.0	19.5	1.529			
	1.00	84.8							
	1.50	83.2							
	2.00	80.1							

* Reference 3.

TABLE 3
Measurements on 1 M glycine with different electrolytic cells

CELL	k	$\epsilon_a - \epsilon_o$	$\kappa_a^d - \kappa_o^d (10^{-6} \text{ohms}^{-1} \text{cm.}^{-1})$		
			65.6 megacycles	32.8 megacycles	16.4 megacycles
No. 1.....	2.96	23.9	20.1	4.7	1.3
No. 2.....	3.59	25.3	21.4	4.7	1.1
No. 3.....	0.706	23.8	20.8	5.1	1.3

values of $\frac{\epsilon_a - \epsilon_o}{C}$ are slightly higher than those given by Hedestrand (13) and by Wyman and McMeekin (22), but considerably lower than those given

by the other investigators. Wyman used wave lengths between 2 and 5 meters. He stated that he could see no dependence of the dielectric constant on wave length in this region. According to our dielectric loss measurements, at a wave length of 2 meters we should expect (compare below) the dielectric constant of the amino acids which we have studied to show a decrease from their long wave length values varying from a fraction of 1 per cent for glycine to a few per cent for ϵ -aminocaproic acid.

The curves representing $\kappa_a^d - \kappa_o^d$ as a function of concentration show increasing slope with increasing concentration. Our measurements at 65.6 megacycles are shown graphically in figure 5.

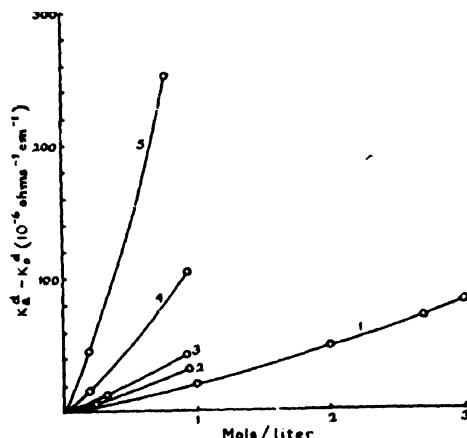


FIG. 5. $\kappa_a^d - \kappa_o^d \sim C$ for (1) glycine, (2) alanine, (3) α -aminobutyric acid, (4) γ -aminobutyric acid, (5) ϵ -aminocaproic acid. Frequency = 65.6 megacycles.

DISCUSSION

It is well known that Debye's theory (4) of dielectrics does not generally apply to fluid systems; in particular the theory fails when applied to systems of high dielectric constant. One reason for this lies in the assumption used for the relation of the polarizing electric force (F) to the external electric force (E), viz.

$$F = E + \frac{4\pi}{3}I$$

(I is the electric moment per unit volume). There is considerable indication that in fluids of high dielectric constant F is approximately independent of the polarization (cf. 16, 17, 21). It seems difficult to account for the near linearity of the relation of dielectric constant to concentration of the amino acid solutions on any other basis, and, as we shall now show, the observed relation of dielectric loss to concentration leads to the same conclusion.

If we assume that F is independent of the polarization, but otherwise

follow the method of calculation used by Debye (4), we obtain (restricting ourselves to low frequencies):

$$\frac{(\kappa_a^d - \kappa_o^d) - \kappa_o^d \frac{\eta_1 - \eta_0}{\eta_0} + \rho \kappa_o^d \frac{\eta_1}{\eta_0}}{(\epsilon_a - \epsilon_o) + \rho(\epsilon_o - n^2)} = \frac{3\eta_1 V}{kT} \omega^2 \frac{10^{-11}}{36\pi} \quad (4)$$

η_1 and η_0 are the viscosities of the amino acid solution and water, respectively; $\rho = C\Phi/1000$ (C = moles per liter; Φ = molal volume of the amino acid); κ_o^d is the specific electric conductance of water resulting from its dielectric absorption (measurements of κ_o^d are recorded below); n is the refractive index of the amino acid (the value of n can be taken as equal to 1.5); V is the volume of the amino acid molecule; k is Boltzmann's constant; and T is the absolute temperature.

In order to test equation 4 we calculate V from this equation and ascertain whether or not the value is independent of the concentration of the amino acid. Since our measurements at 65.6 megacycles are considerably more accurate than those at the lower frequencies, these measurements are used exclusively.

The viscosity of solutions of glycine and alanine was measured by Hedestrand (14). The viscosity of solutions of the other amino acids does not appear to have been determined before, and this characteristic was therefore measured on most of our solutions. The results are shown in table 2.

From the value of V , calculated by means of equation 4, the molal volume $\Phi = 6.0 \times 10^{23} V$ is derived and this value is shown in table 2 under Φ_d . For some of the substances Φ_d decreases slightly with increasing concentration; for others the opposite is true. These variations may be due wholly to experimental errors.

We conclude that equation 4 satisfactorily represents the dependence of $\kappa_a^d - \kappa_o^d$ on concentration. We note that this signifies that the relation of dielectric loss to concentration would also have been linear, as is (to a close approximation) the relation of dielectric constant to concentration, if it were not that the viscosity of the solutions changed with concentration.

Under Φ_i we have shown in table 2 the molal volumes of the amino acids, as given by Cohn (3). The values of Φ_d are generally smaller than Φ_i .

It is of interest to compare the molal volumes obtained from the dielectric measurements with those obtained by using Stokes' law to account for the electric mobility of the ionized amino acid molecules (*viz.*, by taking $6\pi\eta au = 1/300 \times 4.77 \times 10^{-10}$; $\Phi = (4\pi a^3)/3 \times 6.0 \times 10^{23}$; u = velocity of ion per volt centimeter). The mobilities of the glycine and alanine anions and cations were determined by Winkelblech (19), and the values Φ_e shown in table 2 were derived on the basis of his data. The mobilities of the anion and cation are different, and the two mobilities were averaged in carrying through the calculation. We note that Φ_e is still smaller than Φ_d .

The center of the region of anomalous dispersion associated with the amino acid molecule may be expected at the wave length

$$\lambda_m = 2\pi \times 3 \times 10^{10} \frac{(\kappa_a^d - \kappa_o^d) - \kappa_o^d \times \frac{\eta_1 - \eta_2}{\eta_0} + \rho \kappa_o^d \frac{\eta_1}{\eta_0}}{[\epsilon_a - \epsilon_o + \rho(\epsilon_o - n^2)]\omega^2} \times 36\pi \times 10^{11} \text{ cm.}$$

For 1 *M* glycine we obtain $\lambda_m = 8.6$ cm.

The center of the region of anomalous dispersion found by Linhart (15) in solutions of glycine is at a considerably longer wave length. A peculiar circumstance is that he finds the region of anomalous dispersion to lie at about the same wave length for the different amino acids studied. It is difficult to reconcile these results with the results of the present work.

DIELECTRIC ABSORPTION OF WATER

For this measurement, cell No. 4 was constructed identical with cell No. 3, except that the electrodes were placed closer together. The value of *k*

TABLE 4
Dielectric absorption of water

FREQUENCY	$\Delta C \text{ } \mu\mu\text{f}$	$\sigma_4 \times 10^6$	$\sigma_3 \times 10^6$	$\kappa_o^d \times 10^6$
<i>megacycles</i>				
65.6	14.3	60.0	87.7	12.0
32.8	14.3	60.0	65.8	2.8
16.4	14.3	60.0	61.1	0.5

for this cell was 0.280. Cells No. 3 and No. 4 were balanced in the usual way, with dilute solutions of potassium chloride in both, at the different high frequencies. The balance was obtained by varying the concentration of potassium chloride in cell No. 3, while the solution in cell No. 4 was kept constant. We find that when the cells are balanced at a high frequency, the low-frequency electric conductance of the solution in cell No. 3 is higher than in cell No. 4. The reason for this is assumed to be the dielectric absorption of the water. The capacity difference between the cells remains constant at all the different frequencies. The results of a series of measurements are shown in table 4. The difference in capacity between the cells is shown under ΔC and the low-frequency electric conductance of the cells under σ_3 and σ_4 , respectively.

The dielectric constant of water calculated from

$$\epsilon = \frac{36\pi}{10} \Delta C$$

is $\epsilon = 80$ (temperature, 21.0°C.), which agrees well with the generally accepted value.

The specific electric conductance of water, κ_o^d , resulting from its dielectric absorption is obtained from

$$\kappa_o^d = \frac{\sigma_3 - \sigma_4}{(1/k_3) - (1/k_4)}$$

k_3 and k_4 being the values of k for the two cells. κ_o^d varies as the square of the frequency, within the experimental error. Measurement of the dielectric absorption of water was made by Schmelzer (18) at a frequency of 28.4 megacycles. His value for κ_o^d is given as lying between 1.4 and 2.0×10^{-8} ohm⁻¹ cm.⁻¹ (at a temperature of 20°C.).

The wave length λ_m for the center of the region of anomalous dispersion of water may be calculated from

$$\lambda_m = 2\pi \times 3 \times 10^{10} \times \frac{36\pi\kappa_o^d}{(\epsilon_o - n^2)\omega^2} \times 10^{11}$$

n is the refractive index of water in the optical region, $n = 1.3$. If we use the value $\kappa_o^d = 12.0$ obtained at 65.6 megacycles, we derive $\lambda_m = 1.85$ cm. ± 10 per cent. Esau and Baz (9) found by direct observation $\lambda_m = 1.85$ cm. at a temperature of 19.0°C.

SUMMARY

Measurements, at frequencies up to 65.6 megacycles, are given of the dielectric absorption and dielectric constant of different concentrations of solutions of glycine, alanine, α -aminobutyric acid, α -aminocaproic acid, γ -aminobutyric acid, and ϵ -aminocaproic acid. The electrolytic cell containing the amino acid is balanced in a resonance circuit against a similar cell, containing a potassium chloride solution, and a parallel condenser. The errors of the method are discussed in some detail.

The relation of dielectric constant to molar concentration is approximately linear, showing a slight decrease in slope with increasing concentration. In the range of frequencies used, the dielectric absorption (represented by the equivalent electric conductance) increases as the square of the frequency. The relation of dielectric absorption to concentration shows increasing slope with increasing concentration in direct proportion to the change of the viscosity of the solutions with concentration. The results indicate that the relation of polarizing electric force to average electric force in the solutions is approximately independent of the degree of polarization. On this assumption and otherwise following Debye's theory of anomalous dispersion, values of the volume of the amino acid molecules are derived which are somewhat lower than the true volumes. The molecular volumes obtained from the dielectric measurements are closer to the true volumes than those obtained by using Stokes' law to calculate the electric conductance of the amino acid ions.

Measurements are also given of the viscosities of the solutions used and of the dielectric absorption of water.

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A PHOTOGRAPHIC METHOD FOR DETERMINING SMALL DIFFERENCES IN SPECIFIC VOLUME

ROBERT TAFT

Department of Chemistry, University of Kansas, Lawrence, Kansas

AND

LLOYD E. MALM

Department of Chemistry, Utah State Agricultural College, Logan, Utah

Received April 30, 1938

In a study of the electrical conductance of sols and gels of gelatin and of agar, it became necessary to determine whether there is an appreciable difference in the density, or specific volume, in the sol and gel state, i.e., whether or not any contraction or expansion in volume occurs when the solidification of the sol takes place.

A search of the literature gave very little information on this point, most authors tacitly assuming no change in specific volume during the gelation process. The usual methods of determining densities, especially of the material in the solid (gel) state are not satisfactory, because of the difficulty of removing and measuring the mass and volume of a given quantity of gel. Furthermore, we were primarily interested in detecting differences in density, rather than the actual density itself.

Our problem was solved by photographing a specimen of gelatin (or agar) sol in a suitable container before and after it had jelled. A comparison of the resulting negatives enabled us to determine that a slight contraction occurred in passing from the liquid state to the gel state. Further, the method permitted an approximate determination of the difference in density.

The actual procedure involved making a negative of the narrow neck of a 50-cc. pycnometer possessing a diameter of 3.7 mm., which contained the sol in question. To prevent changes in density occurring as a result of temperature difference, the pycnometer was placed in a constant-temperature bath provided with walls of plate glass. The negatives were made with a view camera of long bellows extension, fitted with a lens of 2" focal length. With this arrangement the neck of the flask was projected on the negative at a magnification of 11 diameters. The camera was focussed on the meniscus of the sol, the field including also the defining mark on the neck of the capillary, as will be seen by an inspection of figure 1.



FIG. 1

FIG. 2

FIG. 1. Capillary and meniscus (approximately times four), 7.80 per cent gelatin sol at 30°C.

FIG. 2. Capillary and meniscus (approximately times four), 7.80 per cent gelatin gel at 30°C.

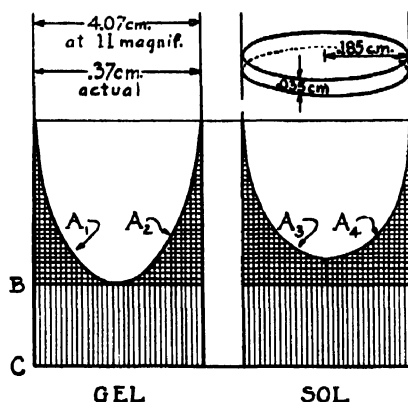


FIG. 3. Diagrammatic illustration of method employed in calculating density change. *C* corresponds to the defining mark on the capillary of the pycnometer; the areas A_1 , A_2 and A_3 , A_4 are so labeled for convenience in counting squares. $(A_3 + A_4) - (A_1 + A_2)$ gives the decrease in vertical cross-sectional area of the sol-gel transformation, measured from the bottom of the gel meniscus. This decrease in area can be converted into its corresponding volume decrease; if the total volume of the pycnometer is known, the percentage contraction can be computed.

Illustration of actual case (figures 1 and 2): $A_1 + A_2 = 225$ squares; $A_3 + A_4 = 324$ squares; the contraction is therefore 99 squares. Since, by measurement, 0.37 cm. was the linear equivalent of 32 squares (each square would thus have an equivalent side of 0.116 cm.), the decrease in volume was approximately a cylinder 0.37 cm. in diameter and $99/32 \times 0.0116$ cm. high. The volume decrease in cubic centimeters is therefore $(3.142)(0.37/2)^2(0.035) = 0.0038$ cc. The total volume of the pycnometer to *B* was found to be 50.071 cc. The contraction on gel formation was therefore $(0.004/50.071 + 0.012) \times 100 = 0.008$ per cent (0.012 cc. is the volume of sol above the line *B*).

The specimen under observation in figure 1 was a gelatin sol of 7.80 (weight) per cent gelatin and had a density of 1.0190 at 30°C., as determined by the usual pycnometric method. It was allowed to remain in the constant-temperature bath for an hour at 30°C., by which time it had set to a firm gel. It was then rephotographed, neither container nor camera having been changed from its original position. The print obtained from the second negative is shown in figure 2. A comparison of figures 1 and 2 shows that the meniscus in the gel state is very noticeably pointed; the meniscus in figure 1 shows the familiar form of all liquids. It is apparent that some contraction has occurred in passing from the liquid state to the gel state. To determine the extent of the contraction, the negatives of figures 1 and 2 were placed on squared paper; then the areas bounded by the meniscus, the walls of the capillary, and the defining mark on the wall of the capillary were carefully traced. From a comparison of these two tracings the change in volume was calculated. The actual method of calculation is shown in figure 3. For the case described it was found that 50 cc. of the liquid underwent a contraction of 0.004 cc.; or the density of the solid (the gel) was 0.008 per cent greater than that of the liquid.

It is recognized, of course, that such a determination is based on the assumption that the volume of the pycnometer is the same before and after gel formation. It is possible that gel formation contracted somewhat the volume of the container, owing to the cohesive forces between gel and glass. No cracks, or other evidences of strain, however, appeared between the glass walls and the gel.

In addition to the determination described in the present paper, other measurements were made, all showing that for gelatin and agar the density of the gel was always slightly greater than that of the liquid form at the same concentration and temperature.

SUPERSATURATION AND LIESEGANG RING FORMATION. I

ANDREW VAN HOOK¹

Department of Chemistry, Lafayette College, Easton, Pennsylvania

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The theory of Liesegang ring formation has been a highly controversial subject ever since the first attempt at an explanation by Wilhelm Ostwald in 1898. E. S. Hedges has summarized the situation up to 1932 (7). He mentions the four most prominent theories advanced to account for the mechanism of construction; while no one theory has been definitely established to the exclusion of the others, the supersaturation ideas of Wilhelm Ostwald (20), as modified by Wo. Ostwald (21) and applied by Hughes (8), seem to be most successful. Apparently the principal obstacle to the more general acceptance of this picture is the want of positive proof of the existence of supersaturation prior to ring formation, especially in view of the fact that rhythmic precipitation occurs in the presence of seeds of the material to be precipitated. Bolam and coworkers (1, 2, 22) have studied very carefully the cases of silver chromate and lead iodide in gelatin and agar in the absence of added seeds, and have definitely demonstrated that true supersaturation does occur in these systems. In the work to be described much of Bolam's work has been confirmed and extended to the case of added seeds. On the basis of the results obtained, a few generalizations regarding some other periodic actions are suggested.

EXPERIMENTAL

For observational purposes the usual Petri dish, test tube, microscope slide, and capillary techniques were used. For quantitative measurements on the silver chromate system the silver electrode was used, and at times the limit of visible precipitation method, as described by Bolam *et al.* (1, 2, 22), was used. In some cases the concentrations were confirmed by analyzing for silver as the chloride and for chromate either colorimetrically or iodimetrically. Most of the experiments were conducted at room temperature; others at controlled temperatures. One batch of chloride- and phosphate-free gelatin, containing 11.1 per cent water, was used throughout the work.

¹ Present address: Department of Chemical Engineering, University of Idaho, Moscow, Idaho.

Crystal seeds were prepared either "externally" or "internally". In the former case the precipitation was conducted under conditions simulating those of the experiment to be performed, washing well, and storing under water. In the latter case an initial excess of inside electrolyte was precipitated directly by the addition of an equivalent amount of inoculant in relatively concentrated solution. The uniform dispersion of these crystal seeds was the most difficult condition to attain. In liquid media the smear (or less successfully, the capillary) technic was used. In the bulk experiments with gels, completely filled tubes were turned continuously end-over-end until gelation occurred.

RESULTS AND DISCUSSION

Many of Bolam's experiments establishing the fact that highly supersaturated solutions of silver chromate in gelatin exist were repeated, and the conclusions reached were the same. In a similar manner it was shown that supersaturated solutions of silver chromate are formed in water, in agar, and in bentonite suspensions.

(1) The solubility of silver chromate in water at 25°C., as determined by approach from both over- and under-saturation, is $1.0 \times 10^{-4}M$. Solutions of silver chromate, 2- to 2.5-fold supersaturated by metathesis, are quite stable, but do equilibrate to the saturation value under the influence of seeds. Several solutions of this strength were kept unaltered for days. At higher supersaturations, however, the stability decreases rapidly; at no time during this work was a solution fivefold or more supersaturated ever observed to have any appreciable permanence. The visibly delayed precipitation of silver chromate upon mixing silver nitrate and potassium chromate solutions is in line with these observations.

(2) Silver chromate seeds were shaken with 1 per cent agar solutions ($10^{-4}M$ in potassium nitrate, $pH = 7.6$) and kept at a temperature of 35°C. in order to maintain the medium fluid. After 3 hr. the concentration reached a constant of $1.05 \times 10^{-4}M$, as determined by the silver electrode. This compares favorably with the aqueous solubility of 1.2×10^{-4} (10). The solubility as determined by the limit of visible precipitation of equivalent amounts of potassium chromate and silver nitrate solutions after 48 hr. aging was $11 \times 10^{-4}M$. Some silver chromate seeds were added to one half of a 1 per cent agar solution $9 \times 10^{-4}M$ in silver chromate, while the second half remained clear. Both solutions were agitated frequently. The analytical results expressing the adjustment of these solutions are given in table 1. Apparently silver chromate in agar solutions supersaturates readily and adjusts slowly, even in the presence of seeds.

(3) Results of the same sort were obtained with silver chromate in 1 per cent bentonite suspensions at room temperature, although in this case

the initial degree of supersaturation was only from four- to six-fold and fell to the equilibrium value during ten days.

The adjustment of supersaturated solutions of silver chromate in 3 per cent gelatin is depicted in figure 1. Increasing the amount of seeding material accelerates the rate of adjustment of these solutions. A sixfold supersaturated, carefully filtered solution of silver chromate in 3 per cent gelatin at 35°C. was divided into twenty well-cleaned and steamed test

TABLE 1
Adjustment of solutions of silver chromate

TIME	SILVER CHROMATE CONCENTRATION—NO SEEDS			SILVER CHROMATE CONCENTRATION—SEEDS (BY SILVER ELECTRODE)
	By silver electrode	By silver chloride	By chromate ion	
<i>days</i>	<i>M</i>	<i>M</i>	<i>M</i>	<i>M</i>
0	8.8×10^{-4}	6.5×10^{-4}	8.5×10^{-4}	8.8×10^{-4}
1	9.1			9.0
2	8.7	10.5	8.3	8.0
5	8.5			8.0
10	8.4			7.0
22	6.0	0.5	5.3	2.0

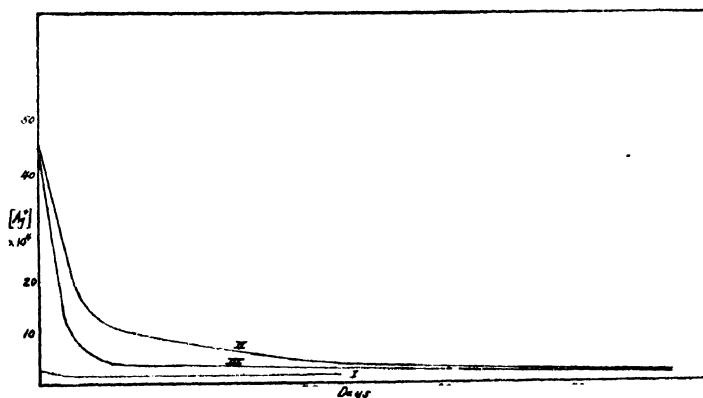


FIG. 1. Rate of adjustment of silver chromate in 3 per cent gelatin solutions after aging for 4 hr. I, saturated with excess solid. II, 44×10^{-4} N in silver nitrate and potassium chromate; no seeds. III, 44×10^{-4} N in silver nitrate and potassium chromate; seeds.

tubes, and sealed with clean corks. Half of these were allowed to set upon cooling overnight to room temperature. At this time four of the liquid and five of the gelled samples had decreased more than 10 per cent of the initial silver concentration. A day later one additional sample from each set had materially decreased in concentration. The previously altered samples continued to decrease in concentration. Of the remaining five liquid and four gelled tubes, three of the former and two of the latter

had decreased in concentration after one week, while the remaining one and two cases, respectively, persisted at their original concentrations for over two weeks. If the original supersaturation is less the persistence is greater, while the reverse is observed for higher concentrations. Seeding promotes the crystallization, and in no case was an original supersaturation retained for more than two days in the presence of seeds.

From numerous experiments representative supersolubilities of silver chromate in various media were calculated, and the results are presented in table 2. These are the values observed after 48 hr. aging, and are

TABLE 2
Representative supersolubilities of silver chromate at room temperature

MEDIUM	METHOD	SILVER CONCENTRATION $\times 10^{-4}$	pH	$H \times 10^{-12}$	$K_{sp.} \times 10^{-12}$
		<i>M</i>			
Water.....	Silver electrode	2.5	7.2	7.8	0.5
	Limit of visible precipitation	11.0	6.4	670	
	Limit of visible precipitation	6.3	6.6	121	
	Limit of visible precipitation	4.5	7.6	52	
1 per cent agar.....	Limit of visible precipitation	11.0	6.5	670	0.6
	Silver electrode	9.0	6.5	365	
1 per cent bentonite..	Silver electrode	5.0		62	
1 per cent gelatin....	Silver electrode	15.0		1690	
3 per cent gelatin....	Silver electrode	15.0	7.6	1690	
5 per cent gelatin....	Silver electrode	18.0	7.8	2940	
	Silver electrode	20.0	6.4	4000	
	Limit of visible precipitation	4.4	5.0	44	4.5
	Limit of visible precipitation	3.9	6.0	29	
	Limit of visible precipitation	5.0	7.0	62	
	Limit of visible precipitation	22.0	7.6	5200	
	Limit of visible precipitation	14.0	7.8	1370	2.4
	Limit of visible precipitation	18.0	7.8	2940	1.3

fairly reproducible under ordinary conditions. The values are not constant over long periods of time, but decrease as already described. The corresponding values of the supersolubility product, H , and the ordinary solubility product, $K_{sp.}$, are included. Corrections for the $\text{CrO}_4^{--} - \text{Cr}_2\text{O}_7^{--}$ equilibrium (11) were made when necessary. The solubility product of silver chromate is linear between 2.28×10^{-12} at 20°C . and 17.9×10^{-12} at 50°C . (10).

The above results are strong confirmation of Bolam's conclusion that true supersaturation of silver chromate in gelatin does occur. The indica-

tions are that the phenomenon is general for the usual Liesegang ring materials and media, but it does not necessarily follow that supersaturation precedes rhythmic precipitation. Both direct and indirect evidence on this point was sought.

Direct method

Hughes (8), Lincoln and Hillyer (14), and Fricke and Suwelack (5) offer analytical results indicating that supersaturation occurs during the formation of a Liesegang ring in the silver chromate-gelatin, copper chromate-silica gel, and magnesium hydroxide-agar systems, respectively, but the conclusion is based on analysis for only one constituent ion, analysis of the clear spaces after ring formation, or involved calculation. It was thought that the conclusion would be more convincing if a locality which was about to have a band deposited were segregated and completely analyzed. Such a section can be accurately defined in space and time by the relationships (12):

$$\frac{h_n}{h_{n-1}} = \text{const.}$$

and

$$\frac{h_n}{\sqrt{t}} = \text{const.}$$

Absolutely clear slabs of gel which were about to have a band of silver chromate precipitated were removed from a 5 per cent gelatin gel containing initially 3.3×10^{-3} moles of potassium chromate per liter. It was ascertained from duplicate experiments that the slabs removed were at least five to eight previous to the last band which would have formed. The following analyses demonstrate irrevocably that the medium is highly supersaturated in silver chromate:

	No. 1	No. 2	No. 3	No. 4	No. 5
$[\text{Ag}^+] \times 10^4$	24.8	60	58	61	42
$[\text{CrO}_4^{2-}] \times 10^3$	1.66	1.66	2.4	2.4	2.9
$H \times 10^{12}$	10,000	60,000	80,000	90,000	50,000

If a small amount of Cl^- is added to the gel before setting, the diffusion wave of Ag^+ ions is indicated by the faint van cloud of precipitated silver chloride. If this section is removed in whole or in part, analysis reveals it to be highly supersaturated in silver chromate.

Indirect method

The only requirement for a supersaturation theory of Liesegang ring formation to be compatible with the fact that rhythmic precipitation can occur in the presence of seeds is that the velocity of crystallization be slow

compared to the rate of growth of rings. Even on this basis there should still be a limiting amount of seeding surface which will prevent ring formation, since the total crystallization depends, among other things, upon the abundance of crystallization centers. In some seeding experiments in water medium, H. W. Morse (18) found that, if the seed crystals are sufficiently close together, periodicity is completely prevented.

Seeds of various materials (silver chromate, lead iodide, lead chromate, mercurous chloride, ferric hydroxide, barium chromate, silver iodide, silver chloride, silver silicate, magnesium carbonate, and calcium carbonate) if present in sufficient amount inhibit the rhythmic precipitation of the same in various media (water, sugar syrups, gelatin, agar, silica gel, and bentonite gel). The same results obtain whether the seeds are prepared externally or internally. The smaller the seeds, the less the quantities required.

A given sample of seeds seems to be equally effective in preventing rhythmic precipitation in different media. For instance, 5.2 to 6.5 millimoles of potassium chromate per liter precipitated by the slow, dropwise addition of an equivalent amount of 0.25*N* silver nitrate in 3 and 5 per cent gelatin, 8 per cent bentonite gel, 1 per cent agar, or in water, in the presence of 16 millimoles per liter unprecipitated, were sufficient to arrest rhythmic precipitation upon inoculating with solid silver nitrate. Likewise 10 to 15 per cent of 0.09 mole of precipitated potassium iodide per liter, either internally or externally, was sufficient to prevent the further periodic precipitation of lead iodide in water, 1 per cent agar, and 8 per cent bentonite. The clarity of the rings was less, and their subsequent deformation and obscuration greater, the closer the amount of seeds to this limiting amount.

Bolam (1, 2) found that the major part of silver chromate in supersaturated solutions is present as a true crystalloid rather than as a protected colloid. The fact that the fraction precipitated and capable of preventing further rhythmic precipitation is independent of the medium and its concentration is more in keeping with Bolam's interpretation than the suggestion of many (see reference 7) that a colloid formation is involved in the deposition of a Liesegang ring. Specifically this uniform behavior makes improbable the suggestion of Notboom (19) and of Dhar and Chatterji (3) that nuclei may fail to release supersaturation because of an adsorbed immobilizing layer of gel. Ghosh (6) affirms the same from his experiments in water medium.

Repeated inoculation of a given gel with small crystals and dispersion of the rhythmically deposited precipitate also leads to the conclusion that there is a limiting concentration of seeds required to prevent banded precipitation. If the silver chromate seeds are prepared outside the test plate, it is only those crystals formed in slightly alkaline environment which prevent rhythmic construction. Seeds prepared in neutral or acid

solution require an inordinate amount or even fail entirely to prevent the Liesegang phenomenon. When one realizes the complexity of the silver-chromate system this is in line with the fact that non-isomorphous seeds fail to prevent rhythmic precipitation while isomorphs do. For example: in gelatin medium approximately the same fraction of carbonate ion precipitated as either lead carbonate or barium carbonate (and sulfate precipitated as lead, strontium, or barium sulfate) prevents the further precipitation of either lead or barium (lead, strontium, or barium) in a periodic manner, whereas barium sulfate, silver chloride, and calcium



FIG. 2. Silver chromate in gelatin medium

oxalate (barium carbonate and silver chloride) seeds have no effect in concentrations of three to six equivalent times as much.

A number of experiments concerning the precipitation of various materials in various media and in the presence of glass powder were performed. In general the same results as those reported by Wo. Ostwald (21) were obtained, namely, that rhythmic precipitation was not prevented. However, as the concentration of glass seeds is increased the rhythmic form of the precipitate becomes more indefinite, and in a few cases it was entirely absent. A single, rather novel result, depicted in figure 2, was obtained

with silver chromate in gelatin medium. There is no indication from the diffusion laws, or from observation, that such a repetition of a series of bands will occur from a single inoculation in a homogeneous system. Such an occurrence would be possible in a heterogeneous system if the crystal seeds inhibiting ring formation were dispersed in a discontinuous manner. Mendhall and Mason (17) report that stratification of settling particles is possible when there is a lateral temperature gradient across the liquid, and it is very likely that this condition was realized during the uncontrolled settling of the specimen illustrated.

Careful microscopic observation during the process of ring growth, in the presence of a concentration of seeds below the critical amount, reveals that the development is more irregular and less definite than in their absence. In the immediate vicinity of a cluster of seeds, ring formation is completely inhibited, so that the formation is only partial. Subsequent alteration (formation of halos) and even complete obliteration are also pronounced.

APPLICATIONS

1. The difficulties of obtaining uniform dispersion of seeds, particularly in water medium, vitiate somewhat the quantitative results obtained. This non-uniform distribution must be either eliminated or evaluated before accurate quantitative results are realized. When this and the evaluation of the differential effects of various variables upon the competing processes of crystal growth and band formation are accomplished, another method for ascertaining the rate of growth of crystals from supersaturated solutions will be made available.

2. McMasters, Abbott, and Peters (16) suggest that there may be a common cause underlying the formation of Liesegang rings, rhythmic banding from melts, and rhythmic crystallization from solution. The picture favored above for Liesegang ring formation may be extended to the other two cases as follows: A melt supercools until the limit of stability is reached at a particular point. Crystallization ensues and spreads about this center. The process is partially adiabatic, so that as growth continues the local temperature rises until a condition is reached when there is an area immediately preceding the crystallization wave front that is no longer supercooled. This corresponds to the period of the rhythm, and the clear space must be traversed before crystallization begins anew. The subsequent alteration and crystallization of this molten section (4, 13, 9) will present a rhythmic appearance of the whole. The case of rhythmic crystallization from solution is explained in a similar manner, with supersaturation due to evaporation and exothermal crystallization being the active agents.

The blotchy appearance of such phenomena is in harmony with the

above interpretation, and the common origin of Fick's law of diffusion and Fourier's treatment of flow of heat is reason for expecting that the three cases should exhibit a common rhythmic appearance.

3. Lloyd and Moravcek (15) report that in addition to the usual two sets of rings formed in the silver nitrate-lead chromate system, there is formed at the air-gel interface a third, ribbon-like, brown set. Such iridescent sets were observed during this work, and they are thought to be secondary in origin as a result of surface tarnishing. They can be leached off readily with dilute nitric acid, and replaced, especially in an atmosphere rich in hydrogen sulfide. The first leachings test strongly for sulfide ion.

SUMMARY AND CONCLUSIONS

1. Silver chromate supersaturates readily in water, gelatin, agar, and bentonite suspension media. Representative values of the supersolubility constant for such solutions are given.

2. These supersaturated solutions return to equilibrium slowly, even in the presence of seeds.

3. The usual Liesegang ring materials supersaturate readily and adjust slowly, yet it does not necessarily follow that supersaturation precedes rhythmic precipitation. The indications that it does are as follows: (a) Direct analysis of sections about to have a Liesegang ring deposited discloses supersaturation of the above order. (b) There is a definite concentration of like or isomorphous seed crystals which prevents rhythmic precipitation. Smaller amounts are ineffective, because the rate of diffusion is high compared to the rate of crystal growth.

4. The compound to be precipitated as a Liesegang ring is present as a crystalloid and not as a complex colloid.

5. The point of view adopted suggests a new method for measuring the rate of growth of crystals from supersaturated solutions.

6. The mechanism of rhythmic crystallization from melts and from solutions is pictured in the same way as the Liesegang phenomenon.

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SUPERSATURATION AND LIESEGANG RING FORMATION. II

ANDREW VAN HOOK¹

Department of Chemistry, Lafayette College, Easton, Pennsylvania

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It has been reiterated (12) that a supersaturation theory of Liesegang ring formation is compatible with the fact that rings are formed in the presence of crystal seeds of the material to be precipitated, if it is assumed that the rate of diffusion is rapid compared to the rate of crystal growth. There should then exist a critical concentration of seeds above which rhythmic precipitation will not occur. This has been observed (7, 12), and for particular conditions it is approximately independent of the medium. For concentrations below the critical the clarity and number of bands should increase as the seed concentration diminishes. This has been confirmed qualitatively, and it is with the quantitative aspects of this variation that this paper deals.

THEORETICAL

The classical case of strong silver nitrate diffusing into dilute potassium chromate may be taken as a model. In the usual experimental arrangement the source of silver nitrate is considered inexhaustible at the concentration of the saturated solution. Counterdiffusion of the weak potassium chromate solution will be neglected in the following simplified treatment.

By Fick's law the amount of silver nitrate diffusing regularly into a volume dx at a distance x from the origin is $D \frac{dc}{dx}$, where D is the diffusion constant. The amount leaving is

$$D \left(\frac{dc}{dx} - \frac{\partial}{\partial x} \frac{dc}{dx} dx \right)$$

or the amount accumulating is $D \left(\frac{d^2c}{dx^2} \right) dx$. This is potentially $\frac{\sqrt{4x^2}}{2} \frac{dx}{dx}$ moles of silver chromate, provided that the chromate-ion concentration is sufficient.

¹ Present address: Department of Chemical Engineering, University of Idaho, Moscow, Idaho.

If crystal seeds of surface s are dispersed uniformly throughout the medium, each one will grow at the rate of

$$\frac{dw}{d\theta} = ks[f(c-c_0)]$$

where $(c-c_0)$ is the supersaturation of silver chromate. The total growth will be $nks[f(c-c_0)]dx$, where n is the seed density. The concentration of silver chromate, c , refers to a state of non-stable equilibrium, and therefore it is reasonable to interpret it in terms of an equivalent concentration of silver nitrate, i.e., potential silver chromate, generated by the incoming silver nitrate. This presumption amounts to neglecting the effect of the inner ion concentration on the rate of growth of the seeds, and seems appropriate in view of the incompletely known form of the rate of crystallization function, and also in view of the approximate experimental results obtained.

The limit of band formation will correspond to the condition when the rate of crystal growth equals the rate at which silver nitrate diffuses into the section: namely,

$$\frac{2nks}{D} [f(c - c_0)] = \frac{d^2c}{dx^2}$$

That the Noyes-Whitney (10) Nernst (9) theory of a unimolecular crystal growth is inadequate is evident from the work of Marc (6), who found that the order varies from unimolecularity to bimolecularity with decreasing temperature. Other workers (1, 2, 4, 5) also find a decided approximate nature for the first-order expression. Therefore, taking

$$f(c-c_0) = (c-c_0)^\alpha$$

empirically, the above equation may be solved by setting $(c-c_0)$ equal to y , and multiplying through by $2dy/dx$:

$$2 \frac{dy}{dx} \cdot \frac{d^2y}{dx^2} = 2 \left(\frac{2nks}{D} \right) y^\alpha \frac{dy}{dx}$$

Integrating:

$$\left(\frac{dy}{dx} \right)^2 = \frac{2}{\alpha + 1} \left(\frac{2nks}{D} \right) y^{\alpha+1} + K_1$$

At $y = 0$, $c = c_0$, and $dy/dx = 0$, whence $K_1 = 0$, and

$$y^{-(\frac{\alpha+1}{2})} dy = \sqrt{\frac{2}{\alpha+1} \left(\frac{2nks}{D} \right)} dx$$

Integrating again and evaluating the constant by means of the condition that $c = a$ constant, B , at $x = 0$ gives the solution in the final form:

$$\left(\frac{1}{(c-c_0)^{(\frac{\alpha-1}{2})}} - \frac{1}{(B-c_0)^{(\frac{\alpha-1}{2})}} \right) = - \left(\frac{\alpha-1}{2} \right) \sqrt{\frac{2}{\alpha+1} \left(\frac{2nks}{D} \right)} x$$

If the criterion of Liesegang ring formation is taken as

$$C = \sqrt{\frac{H}{[\text{CrO}_4^{--}]}}$$

where H is the supersolubility product (3), then when everything but n is held constant, the extent of band formation will be given by $nx^2 = \text{constant}$.

The foregoing analysis is admittedly crude, mainly because of considering the chromate-ion concentration constant and ignoring its counter-diffusion. This complication has been considered² and the correction is deemed unwarranted in view of the necessity of either transforming silver- and chromate-ion concentrations into un-ionized silver chromate concentration, or else expressing the crystal growth equation in terms of these two ion concentrations. Accurate information concerning these operations is not yet available.

EXPERIMENTAL

The relation, $nx^2 = \text{constant}$, was tested with silver chromate in gelatin and in bentonite, lead iodide in agar, and magnesium hydroxide in agar systems. The usual capillary technic, with 1.5-mm. tubing, was utilized. Measurements of the extent of band formation were made to the nearest 0.1 mm. with an ordinary scale and magnifying glass, or to 0.01 mm. by means of a Gaertner micrometer microscope. In all rhythmic precipitation experiments there is a distance, immediately surrounding the point of inoculation, in which the precipitation is general. This "flushing-in" area, preceding the commencement of band formation, increases with the ratio of the concentrations of the reactants. The extent of band formation, x , was usually measured from the head of the series of bands, but since it was not always easy to identify this position (especially as the seed concentration increases), distances in such cases were measured to the point of inoculation and the results plotted in accordance with the modified equation:

$$n(x-a)^2 = \text{constant}$$

No appreciable difference in behavior was observed with seeds prepared and added in three different ways. For preliminary work seeds were precipitated "internally" (12). Externally precipitated seeds were prepared by bringing together the necessary reactants under conditions duplicating the experiment to be performed, and, after thorough mixing, the gel was allowed to set without agitation in a tall cylindrical vessel. Aliquot portions of a narrow horizontal slab were taken for seeding pur-

² Thanks are due Dr. R. Bailey of the Department of Mathematics of Lafayette College for assistance in this task.

poses. The third method consisted in precipitating the respective materials, washing, drying in an oven, and finally powdering. Graded portions were used, usually between 200 and 250 mesh in size.

Each batch of experiments was inoculated simultaneously with an excess of concentrated reactant. Observations on the extent of ring formation were made at various times, and for each set of conditions it was found that there was an optimum period of observation for best results. Beyond this time the rings became indefinite, distorted, and even totally obliterated, owing to secondary effects, while earlier the distance of ring formation was not sufficient for comparative purposes. The best time usually corresponded with the formation of 10 to 20 mm. of rings in a blank experiment.

RESULTS AND DISCUSSION

Representative results are presented in the following log-log plots (figures 1, 2, and 3). The points represent observed values, while the line is placed with a slope of -2 as expected from the equation:

$$\log n + 2 \log x = \text{constant}$$

In general the relation is approximately valid over a considerable portion of the entire range, although serious discrepancies exist. The more serious deviations at large values of n may be associated with the arbitrary assumption of ignoring the chromate-ion diffusion, while at the other extremity the generation and initial rapid growth of new nuclei may be the cause of the deviation.

That the presence of seeds does not seriously influence the fundamental diffusion nature of the Liesegang phenomenon is evident upon application of the Morse and Pierce (8) and Schleusner (11) relations: namely, $h_n/\sqrt{t_n} = \text{constant}, K$; and $h_n/h_{n-1} = \text{constant}, q$, respectively. h and t are the distance and time of appearance of a particular band. For 0.01 M potassium chromate in 5 per cent gelatin with (a) no seeds, (b) "internally" precipitated silver chromate seeds equivalent to 0.001 M potassium chromate, and (c) 0.0025 M seeds, the results shown in table 1 were obtained.

The rapid decrease in the values of k , as banding proceeds, for cases b and c is as expected. If the distance of the diffusion wave front (which is difficult to discern in case c) is employed for h , the values found for k are better:

Case	Values of k	Average
b	4.3; 4.4; 4.2; 4.0; 3.9	4.2
c	5.0; 4.3; 4.5; 4.1; 3.8	4.3

The slight decrease in these values over a distance well beyond that of usual observation indicates that the total diffusion during the time of

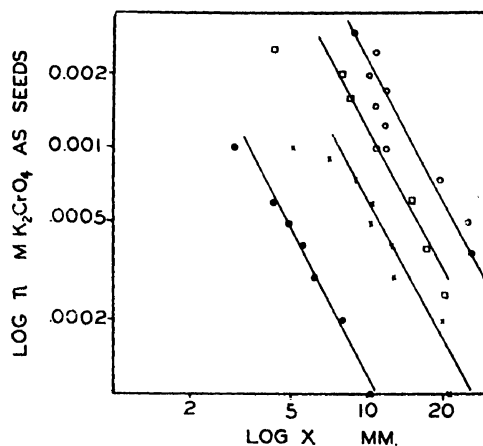


FIG. 1. 0.01 *M* potassium chromate in 5 per cent gelatin. Saturated silver nitrate. Seeds prepared as follows: □, "internally"; ○, "externally"; ×, dry; ●, "externally" in test tube experiment.

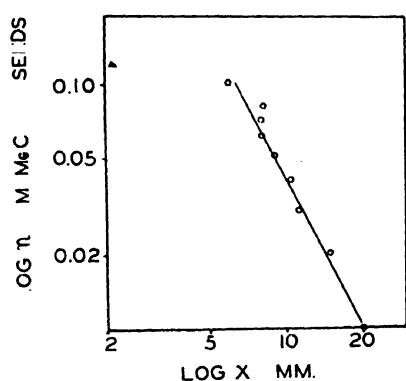


FIG. 2

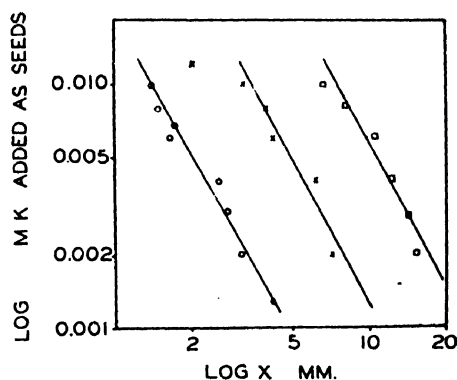


FIG. 3

FIG. 2. 1 *M* magnesium chloride in 1.5 per cent agar. 10 *M* ammonium hydroxide. Seeds prepared "externally".

FIG. 3. 0.1 *M* potassium iodide in 1.5 per cent agar. Half-saturated lead nitrate. Seeds prepared as follows: ○, "internally"; ×, "externally"; □, dry.

TABLE 1
Values of *q* and *k*

CONSTANTS	CASE	VALUES	AVERAGE
<i>q</i>	<i>a</i>	1.11; 1.08; 1.06; 1.11; 1.11; 1.10	1.10
	<i>b</i>	1.06; 1.12; 1.05; 1.07; 1.09; 1.08	1.08
	<i>c</i>	1.01; 1.05; 1.03; 1.06; 1.05; 1.04	1.04
<i>K</i>	<i>a</i>	4.49; 4.45; 4.55; 4.50	4.50
	<i>b</i>	4.2; 4.40; 4.2; 3.28	
	<i>c</i>	4.9; 4.51; 4.2; 2.4	

interest is little disturbed by the presence of seeds. That is, the number added is negligible compared to the number generated in the formation of a definite and distinct Liesegang band. Simultaneously with the above observations (extending over a distance of 30 to 50 mm. and up to 60 hr.), it was noted that the chromate-ion concentration remained undisturbed at a distance of only 2 to 5 mm. ahead of the diffusion wave front. In the capillaries used it would have been possible to detect visibly a variation of 10 to 15 per cent in concentration. This makes the early assumption of ignoring counterdiffusion of potassium chromate more agreeable.

According to the original complete expression, nsx^2 should be constant. Since s is proportional to the average size squared, then $nL^2x^2 = \text{constant}$; or if n is held constant, L and x should vary in an inverse manner. This was found to be only qualitatively true, x being less dependent on L than indicated.

SUMMARY AND CONCLUSIONS

The extent of Liesegang ring formation (x) in the presence of crystal seeds of the material precipitating is found to decrease rapidly as the number of nuclei (n) increases.

Over a limited range there is approximate confirmation of the expression $nx^2 = \text{constant}$. More exact information on the effect of ion concentrations on the rate of growth of slightly soluble substances is necessary for a more complete form of the above expression.

The initial presence of crystal seeds does not alter the fundamental diffusion nature of the Liesegang phenomenon.

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THE SURFACE TENSION-VISCOSITY RELATION

C. A. BUEHLER

Department of Chemistry, University of Tennessee, Knoxville, Tennessee

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The surface tension and viscosity are two easily found physical constants which have been employed with some success in the determination of the structure of chemical compounds. Unlike many other physical properties, both appear in equations which, when applied to many organic compounds, give constant values regardless of the temperature. Because of this fact, a comparison of these equations becomes of interest in that it points out a relation between the surface tension and viscosity somewhat simpler than those (3, 4) previously advanced.

The surface tension appears in the well-known parachor equation in which P , the parachor, may be expressed, at temperatures removed from the boiling point, as

$$P = \frac{M\gamma^{\frac{1}{3}}}{D} \quad (1)$$

where M is the molecular weight, γ the surface tension, and D the density of the liquid. Recently Souders (5) has advanced a similar equation in which the viscosity appears:

$$I = \frac{M}{D} (\log_{10}(\log_{10}\eta) + 2.9) \quad (2)$$

Here I is the viscosity-constitutional constant and η is the viscosity. Since the data compiled in table 1 show that

$$1.2P = I$$

it follows from equations 1 and 2 that at the same temperature, since the densities are equal,

$$\gamma^{\frac{1}{3}} = \frac{\log_{10}(\log_{10}\eta) + 2.9}{1.2}$$

or

$$\log_{10}(\log_{10}\eta) = 1.2\gamma^{\frac{1}{3}} - 2.9$$

The compounds selected in table 1 are those for which the parachor is independent of the temperature. Alcohols, phenols, amines, and carboxylic acids, all of which exhibit an increase in parachor with a tempera-

ture rise, were intentionally omitted. The variations shown in I/P are doubtless due to inaccuracies in the physical constants involved, yet it is

TABLE 1
Parachor and viscosity-constitutional constants

COMPOUND	P	I^*	I/P
Hexane.....	271.0†	340	1.25
Heptane.....	310.8†	393.5	1.27
Octane.....	350.7†	449	1.28
Decane.....	430.6†	561	1.30
Benzene.....	207.5‡	249.8	1.20
Toluene.....	246.5‡	296.2	1.20
Ethyl benzene.....	285.4‡	344.7	1.21
<i>o</i> -Xylene.....	283.3§	347	1.22
<i>m</i> -Xylene.....	284.5¶	343.5	1.21
<i>p</i> -Xylene.....	284.5¶	346.0	1.22
Naphthalene.....	312.5§	376.6	1.21
Methyl iodide.....	146.2†	170	1.16
Ethyl bromide.....	165.7†	198.5	1.20
Ethyl iodide.....	187.0†	225.5	1.21
Propyl chloride.....	190.4†	232	1.22
Propyl bromide.....	205.3†	250	1.22
Propyl iodide.....	226.0†	276.5	1.22
Isopropyl bromide.....	205.1§	257	1.25
Isobutyl chloride.....	228.4§	286	1.26
Isobutyl bromide.....	243.8§	303	1.24
Chlorobenzene.....	244.2¶	290.5	1.19
Bromobenzene.....	257.9¶	307.5	1.19
Ethyl ether.....	211.8§	257.0	1.21
Acetone.....	161.5§	191.5	1.19
Methyl ethyl ketone.....	199.5¶	241.5	1.21
Diethyl ketone.....	236.2§	288.5	1.22
Nitrobenzene.....	263.3§	308.5	1.17
<i>m</i> -Nitrotoluene.....	298.8§	358.9	1.20
Ethyl formate.....	177.7§	215.5	1.21
Methyl acetate.....	177.0§	211.5	1.19
Ethyl acetate.....	216.5‡	265.5	1.23
Propyl acetate.....	257.0‡	321.5	1.25
Mean.....			1.22

* Values are from reference 5. When a range is given, the intermediate value has been used.

† Values are from reference 2.

‡ Values are from reference 1.

§ Brit. Assoc. Advancement Sci. Rep. 1932, 265-83. When several values are given, a mean was used.

¶ Unpublished results of this laboratory.

interesting to note that there seems to be a tendency for this constant to increase as the carbon chain lengthens.

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THE SOLUBILITY OF NITROGEN AND ARGON IN SEA WATER¹

NORRIS W. RAKESTRAW AND VICTOR M. EMMEL

Woods Hole Oceanographic Institution, Woods Hole, Massachusetts

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INTRODUCTION

We recently described a method for the determination of dissolved nitrogen in sea water (4), in which the air is removed from the water sample *in vacuo* and the oxygen, nitrogen, and inert gas residue are measured separately. In making such determinations on actual sea water it is often necessary to compare the values obtained with the equilibrium solubility of nitrogen from the atmosphere. The only figures available for such comparison are those obtained by Fox (2, 3), which have never been seriously questioned. Using these for comparison, however, our analyses consistently indicated an unsaturated condition of water from nearly all sources, with respect to gaseous nitrogen. Believing this to be unlikely, and convinced of the accuracy of our own method, we undertook a re-determination of the solubility of nitrogen in sea water of different temperatures and chlorine contents, within the range ordinarily encountered.

Fox's method consisted in the measurement of the volume of "atmospheric nitrogen" absorbed by a fixed volume of water from a known total volume of the gas. This requires a correction for the argon content of the "atmospheric nitrogen," which can probably be made with sufficient accuracy for our purpose, even though the absorption coefficient of argon in sea water is not well known. But in addition to this, considering the use to which these figures are to be put, it would seem preferable to let the water come into complete equilibrium with the actual atmosphere, rather than with nitrogen alone, and to determine the dissolved nitrogen directly, assuming a constant composition of the atmosphere. The results of such a procedure, described below, are slightly lower than those of Fox (corrected for argon), but are more consistent with the nitrogen content which we find in sea water in nature.

Examining Fox's method more closely, we suspected that his systems might have been supersaturated. He saturated the water by vigorous shaking for several minutes, followed by only a short period of standing, until the pressure became constant. We have found that on shaking sea

¹ Contribution No. 175 from the Woods Hole Oceanographic Institution.

TABLE 1
Experimental data

CHLORINE CONTENT	SAMPLE*	EQUILIBRIUM TEMPERA- TURE	EQUILIBRIUM PRESSURE	MEASURED VOLUME		EQUILIBRIUM SOLUBILITY AT 760 MM. ATMOSPHERIC PRESSURE IN MILLILITERS PER 1000 ML. OF WATER	
				Nitrogen	Residue	Nitrogen	"Argon"
<i>grams per kilogram</i>		<i>°C.</i>	<i>mm.</i>	<i>ml.</i>	<i>ml.</i>	<i>ml.</i>	<i>ml.</i>
16.03	A	2.11	766.3	1.434		14.22	
	A	7.08	758.7	1.262	0.0356	12.68	0.352
	B	7.08	758.7	1.262	0.0346		
	A	12.15	767.0	1.160	0.0317	11.53	0.312
	B	12.15	767.0	1.162	0.0312		
	A	18.03	765.5	1.038	0.0289	10.33	0.288
	B	18.03	765.5	1.041	0.0290		
	A	25.05	764.0	0.925	0.0242	9.19	0.240
	B	25.05	764.0	0.920	0.0244		
	A	2.11	767.0	1.394		13.81	
18.00	A	7.08	758.7	1.283	0.0339	12.40	0.341
	B	7.08	758.7	1.234	0.0340		
	A	12.15	766.3	1.134	0.0301	11.27	0.303
	B	12.15	766.3	1.134	0.0309		
	A	18.03	768.5	1.016	0.0274	10.05	0.270
	B	18.03	767.7	1.015	0.0272		
	A	25.05	763.2	0.903	0.0237	9.00	0.236
	B	25.05	762.5	0.903	0.0236		
	A	2.11	767.0	1.363		13.50	
	A	7.08	758.7	1.203	0.0338	12.08	0.332
19.99	B	7.08	758.7	1.201	0.0324		
	A	12.15	766.3			10.95	0.296
	B	12.15	766.3	1.103	0.0298		
	A	18.03	764.7	0.991	0.0271	9.89	0.266
	B	18.03	764.7	0.997	0.0265		
	A	25.05	762.5	0.880	0.0226	8.81	0.227
	B	25.05	762.5	0.886	0.0230		

* Sample A was saturated with air at a temperature above the equilibrium temperature; sample B at a temperature below.

water with air and allowing to stand until the air bubbles are no longer visible, the nitrogen content is regularly about 2 per cent higher than the equilibrium value at that temperature. It has long been known that the surface water of the sea may be supersaturated with air, from the abnormal solubility of fine bubbles of foam. We are of course in no position to urge that the difference between our solubility values and those of Fox is entirely due to this.

METHOD

Samples of natural sea water containing approximately 16, 18, and 20 g. of chlorine per kilogram were prepared by dilution from the highest concentration. Duplicate portions, of about 250 ml., were placed in

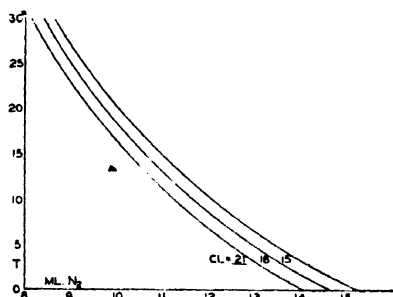


FIG. 1

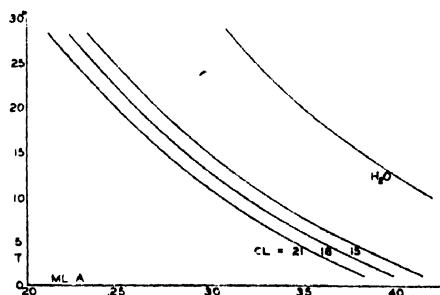


FIG. 2

FIG. 1. Solubility of nitrogen in sea water of different chlorine contents and temperatures. Solubility is expressed in milliliters of gas (at standard temperature and pressure) per liter of water, in equilibrium with air at 760 mm.

FIG. 2. Solubility of "argon" (total inert gas in atmosphere) in sea water of different chlorine contents and temperatures. Solubility is expressed in milliliters of gas (at standard temperature and pressure) per liter of water, in equilibrium with air at 760 mm. The curve for the solubility in pure water is taken from results of Estreicher (1).

citrate bottles, one of these warmed to about 30°C. and the other cooled to about 8°C., and both shaken for 30 min. to saturate them with air. They were then placed in a thermostat at 25°C. for 18 hr. to come to equilibrium, open to the air, with occasional but not too vigorous agitation. Both samples were then analyzed for nitrogen. The same was done at temperatures of 18°, 12°, 7°, and 2°C., the duplicate portions being always saturated at temperatures above and below the final equilibrium temperature, except in the case of the lowest one, in which this was not possible. It may safely be assumed that complete equilibrium was reached in this latter instance also, in view of the satisfactory agreement of the two samples at all other temperatures.

The data are given in table 1. The barometric pressure is included,

from which, in the last column, is calculated the equilibrium solubility in contact with a normal atmosphere of 760 mm.

It was thought worth while to measure the residual gas, after removal of carbon dioxide, oxygen, and nitrogen, and to include this as "argon,"

TABLE 2

Solubility of nitrogen in sea water

Expressed in milliliters (at standard temperature and pressure) per liter of water, from a normal atmosphere of 760 mm.

CHLORINE CON- TENT.....	15	16	17	18	19	20	21
TEMPERATURE	SOLUBILITY						
°C.	ml.	ml.	ml.	ml.	ml.	ml.	ml.
0	15.22	15.02	14.82	14.61	14.40	14.21	14.01
1	14.81	14.61	14.42	14.23	14.04	13.85	13.66
2	14.43	14.24	14.06	13.88	13.69	13.51	13.33
3	14.07	13.89	13.72	13.54	13.36	13.19	13.01
4	13.73	13.56	13.40	13.24	13.06	12.89	12.72
5	13.43	13.26	13.10	12.94	12.78	12.62	12.45
6	13.14	12.98	12.82	12.67	12.51	12.35	12.19
7	12.88	12.72	12.56	12.41	12.26	12.10	11.95
8	12.62	12.47	12.32	12.17	12.02	11.87	11.71
9	12.38	12.23	12.08	11.94	11.79	11.64	11.49
10	12.15	12.00	11.86	11.71	11.56	11.42	11.27
11	11.92	11.78	11.63	11.49	11.34	11.20	11.06
12	11.69	11.56	11.42	11.28	11.13	10.99	10.85
13	11.47	11.34	11.21	11.07	10.93	10.79	10.65
14	11.25	11.13	10.99	10.86	10.73	10.59	10.45
15	11.04	10.92	10.79	10.66	10.53	10.39	10.26
16	10.83	10.72	10.59	10.47	10.34	10.21	10.08
17	10.63	10.52	10.40	10.28	10.15	10.03	9.91
18	10.44	10.33	10.21	10.10	9.98	9.86	9.74
19	10.26	10.15	10.03	9.92	9.81	9.69	9.58
20	10.08	9.98	9.87	9.76	9.65	9.54	9.43
21	9.91	9.82	9.71	9.61	9.50	9.39	9.28
22	9.75	9.66	9.56	9.46	9.35	9.24	9.14
23	9.60	9.51	9.41	9.31	9.20	9.10	9.00
24	9.45	9.36	9.26	9.16	9.06	8.96	8.86
25	9.30	9.21	9.11	9.02	8.92	8.82	8.73
26	9.16	9.07	8.97	8.88	8.79	8.69	8.60
27	9.02	8.94	8.84	8.75	8.66	8.56	8.47
28	8.89	8.84	8.72	8.62	8.53	8.44	8.35

although these figures are of a distinctly lower order of accuracy. This crude fraction of inert gas will therefore be designated as argon, although obviously impure. These figures were obtained by measuring the pressure of the residual gas, when contained in the capillaries between the stopcocks

1, 2, and 3 in the apparatus, shutting off the reservoir C, ordinarily used during the measurement of the oxygen and nitrogen.

Plotting the nitrogen and argon content against chlorine content, at different temperatures, gave a series of straight lines, from which points were taken for the construction of the curves in figures 1 and 2. From these curves tables 2 and 3 have been constructed.

TABLE 3

Solubility of "argon" in sea water

Expressed in milliliters (at standard temperature and pressure) per liter of water, from a normal atmosphere of 760 mm.

CHLORINE CON- TENT.....	15	16	17	18	19	20	21
TEMPERATURE	SOLUBILITY						
°C.	ml.	ml.	ml.	ml.	ml.	ml.	ml.
2	0.405	0.400	0.395	0.389	0.384	0.379	0.373
4	0.384	0.379	0.374	0.369	0.363	0.358	0.352
6	0.365	0.360	0.355	0.350	0.345	0.340	0.335
8	0.347	0.343	0.338	0.333	0.329	0.324	0.319
10	0.331	0.327	0.323	0.318	0.314	0.310	0.305
12	0.317	0.313	0.309	0.304	0.300	0.296	0.292
14	0.304	0.300	0.296	0.292	0.288	0.284	0.280
16	0.292	0.288	0.284	0.280	0.277	0.273	0.269
18	0.282	0.278	0.274	0.270	0.267	0.263	0.259
20	0.272	0.268	0.264	0.260	0.256	0.253	0.249
22	0.262	0.258	0.255	0.251	0.247	0.244	0.240
24	0.253	0.249	0.246	0.242	0.238	0.235	0.231
26	0.244	0.240	0.237	0.233	0.229	0.226	0.222
28	0.235	0.231	0.228	0.224	0.220	0.217	0.213

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THE OXIDATION-REDUCTION POTENTIALS OF UNSTABLE ORGANIC SYSTEMS¹

A. E. CAMERON

Kodak Research Laboratories, Rochester, New York

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The determination of the oxidation-reduction potential of a system requires that the two forms be present and in thermodynamic equilibrium under the conditions of the experiment. The rapidity with which the oxidized forms of most photographic developing agents are converted into other compounds, particularly in alkaline solution, makes direct measurements upon a mixture of reduced and oxidized forms uncertain. Fieser (5, 7, 8) introduced a method of making oxidation-reduction measurements upon such systems, based upon the experimental fact that the oxidized forms of many irreversible systems have a definite but short life in solution. When enough oxidizing solution is added to the reduced form of such a system to produce a half-oxidized mixture, and the readings of the observed potential of a noble metal electrode are plotted as a function of time, it is frequently possible to extrapolate to zero time and thus determine the potential of the mixture before alteration in the concentration of the oxidized form takes place.

This paper is the result of the application of Fieser's method to measurements upon certain organic systems of interest to photographic theory.

EXPERIMENTAL

The *p*-methylanilinophenol sulfate used was the photographic product Elon, manufactured by the Eastman Kodak Co. This was given the purification treatment outlined by Schering (13) to eliminate any *p*-aminophenol present. A hot saturated solution of *p*-methylanilinophenol sulfate in dilute acetic acid was treated with benzaldehyde, allowed to cool, the crystals filtered off, and a second crop of crystals thrown out by addition of acetone. Two recrystallizations were carried out from dilute sulfuric acid solution, with rejection of the first small crop of crystals formed in each case.

The monosulfonic acid of *p*-methylanilinophenol was prepared by T. H. James of these laboratories by heating it with sulfuric acid for 8 hr. on a water bath and pouring it into water. No further purification

¹ Contribution No. 660 from the Kodak Research Laboratories.

was carried out, other than a thorough washing of the precipitate. The hydroquinone used was the photographic product manufactured by the Eastman Kodak Co., and the hydroxyhydroquinone was twice recrystallized before use.

All buffer salts used were of reagent quality from reliable manufacturers, as was the potassium ferricyanide used as oxidizing agent. For measurements in acid solutions it was found necessary to prepare potassium molybdicyanide. In this preparation the directions of Fieser (6) were followed. The oxidizing solutions were stored in dark glass bottles wrapped in opaque cloth.

The nitrogen used to maintain an inert atmosphere was taken from a commercial cylinder of compressed gas. Gas from the cylinder was passed through two towers of solid ammonium carbonate, and then through a tower of soda lime, leaving a definite partial pressure of ammonia in the gas. The mixture was passed through a quartz tube packed with platinized asbestos free from sulfur and heated to 450–500°C. Ammonia remaining after the reaction of ammonia and oxygen was removed with wash towers of 30 per cent sulfuric acid colored with bromophenol blue to indicate exhaustion, and acid spray and carbon dioxide were removed with a wash of 60 per cent potassium hydroxide. A bottle of a 0.1 per cent solution of reduced indigodisulfonate in the line indicated complete absence of oxygen, even at high rates of flow. It is important to insure saturation of the gas stream with ammonia, however. Exhaustion of any reagent was readily noted, and the line could be operated for long periods of time without attention.

Solutions of the compounds investigated were made up in 0.02 *M* concentration and stored in clear glass flasks in an atmosphere of hydrogen. The flasks were arranged so that the solutions could be delivered to water-jacketed, 10-ml. burets without destroying the protective atmosphere. The *p*-methylaminophenol and the monosulfonic acid both showed some sign of decomposition, even in acid solution. They gradually acquired a brownish-red coloration. This decomposition did not proceed to the point where a change in titer could be noted.

The reference half-cell and bridge employed in the pH determinations and in the oxidation-reduction potential measurements were 3.5 *N* in potassium chloride. This solution was prepared volumetrically at 20°C. This half-cell was assigned the value of 0.2502 volt against the normal hydrogen electrode at 20°C., and this value was used throughout the calculations.

APPARATUS

The essential parts of the apparatus are outlined in figure 1. A double-walled beaker, the top of which was flattened and ground plane, was

fitted with a flanged glass cap, also ground plane, which carried a water seal for the stirrer, a glass electrode, and a neck in which could be inserted a stopper carrying the platinized electrodes, or blank platinum and gold electrodes. Lead-in tubes for the salt bridge and for the gas supply to a porous alundum bubble head were sealed through the cap. Three small necks on the cap permitted insertion of buret tips with pieces of small rubber tubing for gasketing. A thermometer mounted in this same cap permitted the determination of the temperature of the reaction mixture. Water was pumped through the jackets of the reaction vessel, the half-cell, and the burets from a 35-gallon thermostat operating at $20^{\circ}\text{C.} \pm 0.01^{\circ}$.

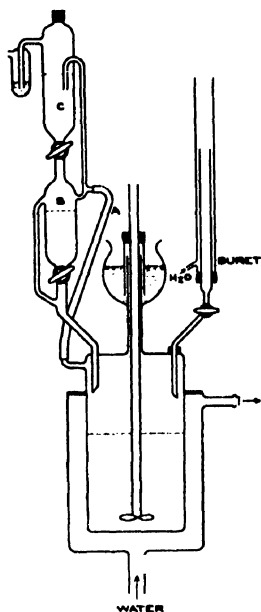


FIG. 1. The apparatus

The addition tube, shown in figure 1, made it possible to add the oxidizing solution rapidly and flush the vessel with buffer solution without admitting atmospheric oxygen. With the pinch clamp on the rubber tubing, A, nitrogen from the reaction vessel swept out compartment B, containing the oxidizing solution, and bubbled through the buffer solution in compartment C, before escaping to the air through the bubbler. When the clamp was removed from the tubing, nitrogen from the reaction vessel could replace the solutions when the lower and upper stopcocks were opened in succession. The stopcocks were both of large bore to permit 10 ml. of solution to be added in about 2 sec.

The experimental procedure followed consisted in adding 100 ml. of buffer solution, 0.2 M in buffering ion and with a sodium-ion concentra-

tion fixed by addition of sodium sulfate, as necessary, to the reaction vessel, and determining the pH with two hydrogen electrodes. The glass electrode was then read, and the hydrogen displaced with pure nitrogen with the substitution of blank platinum and gold electrodes for the platinized ones. The addition tube was set in place with the measured amount of oxidizing solution and buffer solution for flushing, and half an hour allowed for the sweeping out of hydrogen and air. Ten milliliters of reducing agent was then added from one of the jacketed burets. The lower stopcock of the addition tube was opened, and at the same time an electric timer was started which gave a single stroke on a bell at 15-sec. intervals.

TABLE 1
p-Methylaminophenol, 50 per cent oxidized, at 20°C.

pH	<i>E'</i>	pH	<i>E'</i>
	<i>volts</i>		<i>volts</i>
0.96	0.6869	8.57	0.1884
1.37	0.6574	9.14	0.1552
2.10	0.6182	9.32	0.1465
2.59	0.5919	9.52	0.1352
3.38	0.5402	9.81	0.1240
3.86	0.5122	9.93	0.1130
4.32	0.4762	10.33	0.0934
4.66	0.4463	10.36	0.0930
4.81	0.4309	10.47	0.0892
4.90	0.4301	10.75	0.0820
5.28	0.3960	10.81	0.0745
5.78	0.3574	10.85	0.0732
5.80	0.3582	11.02	0.0702
6.40	0.3220	11.30	0.0602
7.00	0.2820	11.35	0.0560
8.10	0.2202	11.69	0.0452
8.13	0.2135	11.97	0.0370
8.14	0.2132	12.18	0.0319
8.25	0.2040	13.03	0.0052
8.41	0.1990	13.60	-0.0118

The upper stopcock was then opened and the lower chamber flushed into the reaction vessel.

Readings were taken at 15-sec. intervals for 3 min. and at 1-min. intervals for 7 min. The glass electrode was then read again, and the pH of the solution as originally determined with the hydrogen electrode was corrected for any change in pH which had occurred. Readings were taken with a student-type potentiometer. The potential of the glass electrode was read with the same potentiometer, using a ballistic galvanometer and a 1 microfarad condenser as null point indicator.

Addition of the solutions raised the temperature of the reaction mixture slightly, but this effect could be disregarded, since in most cases the

extrapolation to zero time was made from a graph which was a straight line up to 10 min.

The *p*-methylaminophenol and sulfonic acid solutions were standardized against the oxidizing solutions by discontinuous titrations, a run being

TABLE 2
p-Methylaminophenolsulfonic acid, 50 per cent oxidized, at 20°C.

pH	<i>E'</i>	pH	<i>E'</i>
	<i>volts</i>		<i>volts</i>
1.03	0.7323	5.59	0.4062
1.58	0.7000	6.62	0.3422
2.05	0.6729	7.05	0.3194
2.54	0.6414	8.44	0.2359
2.73	0.6224	9.21	0.1942
3.90	0.5389	9.77	0.1622
4.23	0.5102	10.31	0.1317
4.48	0.4902	10.70	0.1175
4.87	0.4585	11.39	0.0902
4.92	0.4542	11.45	0.0890
5.26	0.4229	11.81	0.0774

TABLE 3
Benzohydroquinone, 50 per cent oxidized, at 20°C.

pH	<i>E'</i>	pH	<i>E'</i>
	<i>volts</i>		<i>volts</i>
6.28	0.3342*	11.32	0.0957
6.33	0.3374	11.34	0.0945
7.03	0.2982	11.54	0.0874
7.17	0.2900	11.60	0.0888
8.01	0.2370	11.61	0.0872*
8.97	0.1844	11.85	0.0820
9.64	0.1469	12.00	0.0788
10.36	0.1209	12.30	0.0704
10.41	0.1189	12.36	0.0664*
10.43	0.1172	12.43	0.0664†
10.67	0.1104	12.55	0.0560*
10.86	0.1025	12.78	0.0370*
11.06	0.1022	12.81	0.0453
11.32	0.0916	13.01	0.0302*

* By addition of quinhydrone solution.

† By addition of quinone solution.

made for each point on the titration curve. The hydroquinone solution was standardized by direct titration at a pH at which decomposition of the quinone did not interfere, and the hydroxyhydroquinone solution was standardized by rapid titration at pH 0.5, and by a discontinuous titration.

DATA

The data for *p*-methylaninophenol and *p*-methylaninophenolsulfonic acid are given in tables 1 and 2.

Table 3 contains the data obtained from an attempt to carry the measurements of the oxidation-reduction potential of the hydroquinone system up into the alkaline range where the quinone is unstable. The data, other than those specially marked, were obtained by the addition of sufficient ferricyanide solution to produce a half-oxidized mixture, or by selecting the midpoint of the titration with a ferricyanide solution in the lower pH range.

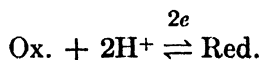
Attempts were made to investigate the oxidation-reduction potential of hydroxyhydroquinone over a considerable range of pH. The data for these measurements appear in table 4.

TABLE 4
Hydroxyhydroquinone, 50 per cent oxidized, at 20°C.

pH	<i>E'</i> volts	pH	<i>E'</i> volts
0.50	0.5707	4.20	0.3310
1.26	0.5310	4.24	0.3490
2.30	0.4690	4.62	0.3217
2.76	0.4394	5.32	0.2542
3.40	0.3896	5.86	0.2102
3.58	0.3740	6.04	0.1840
3.76	0.3690	6.75	0.1255
3.87	0.3487	7.30	0.0802
4.06	0.3797		

DISCUSSION

The equilibrium between the oxidized and reduced forms of *p*-methylaninophenol may be formally represented by the following expression:



The participation of hydrogen ions in the equilibrium and the possibilities of ionization of the secondary amino groups in both reduced and oxidized forms renders the system rather complicated. An expression which was derived and found to fit the experimental data with pleasing exactitude was the following:

$$E = E_0 - 0.029 \log_{10} S_R/S_O - 0.029 \text{ pH} \\ - 0.029 \log \frac{K_w + K_o[\text{H}^+]}{K_a K_w + K_w[\text{H}^+] + K_R[\text{H}^+]^2}$$

In this expression E_0 is a constant which is characteristic of the system, S_R and S_O are the total concentrations of reduced and oxidized forms, K_w is the ionization constant of water at 20°C., K_a is the acid ionization of the phenolic group in the reduced form, and K_o and K_R are the apparent basic ionization constants of the secondary amino groups in oxidized and reduced forms. The basic ionization constants are defined for the oxidized form by the expression:

$$K_o = \frac{[\text{Ox}^-]K_w}{[\text{Ox}][\text{H}^+]}$$

and by a similar expression for the reduced form. In $[\text{Ox}]$ and $[\text{Red}]$ are included the concentrations of both hydrated and unhydrated un-ionized forms.

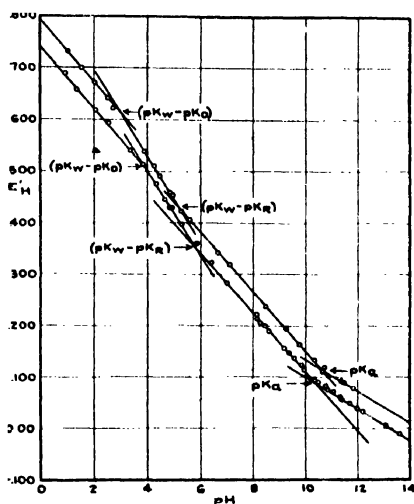


FIG. 2

FIG. 2. The oxidation-reduction potential of *p*-methylaminophenol (lower) and *p*-methylaminophenolsulfonic acid (upper) in equilibrium with their oxidants at 20°C.

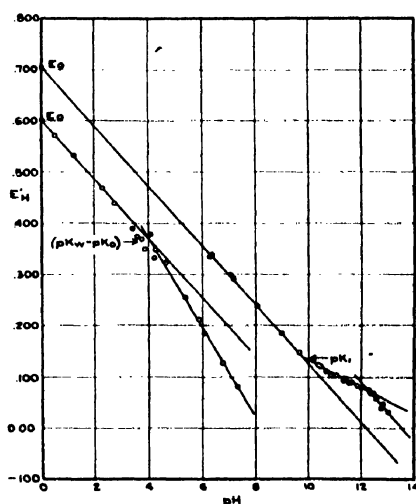


FIG. 3

FIG. 3. The oxidation-reduction potential of benzohydroquinone (upper) and hydroxyhydroquinone (lower) in equilibrium with their quinones at 20°C.

Figure 2 shows the graphs of the data for both systems. In these graphs the lines are drawn with theoretical slopes, and the constants given in table 5 were used in the calculations. It will be noted that the data fit the calculated lines with excellent regularity.

Data from other sources are included for purposes of comparison. Fieser found that, working in the presence of air, he was not able to carry the measurements above pH 8 before the rate of decomposition of the oxidized form became so rapid that extrapolation to zero time of the

potential-time plot was impossible. In the present work it was found possible to carry the measurements into quite alkaline solutions before the decomposition became too rapid. In all measurements of both compounds, the graph of the potential against time was found to be a straight line for a considerable period. In some cases it remained a straight line up to 15 min. This indicated, since the drift was toward lower potentials, that the oxidized form was decreasing in concentration by a reaction whose rate was unimolecular.

The mechanism of this decomposition has been discussed by Fieser, but no direct data appear to be available. In the range of pH from the pK_0 of the two compounds up to pH 8.0, the decomposition leads to the formation of a purple compound. In lower ranges of pH the iminoquinone was yellow. The purple color appeared to develop as a function of time, indicating that it was due to a combination of the decomposition product of the iminoquinone with either the iminoquinone or the reduced form of the system. The combination with the iminoquinone appeared

TABLE 5
Constants used in the calculations

	<i>p</i> -METHYLAMINOPHENOL		<i>p</i> -METHYLAMINOPHENOL-SULFONIC ACID
E'_{pH}	0.7402 volt		0.7920 volt
E_0	0.6888 volt	0.6877 volt (5)	0.7292 volt
K_0	6×10^{-11}	1×10^{-10} (5)	5.88×10^{-12}
K_R	3.54×10^{-9}	1×10^{-8} (5)	8.50×10^{-10}
K_a	4×10^{-11}	6.45×10^{-11} (14)	2.51×10^{-11}
K_w	6.16×10^{-15} (10)		6.16×10^{-15} (10)

to be the more likely, for titration of the mixture with sodium sulfite, which removed the oxidized form as monosulfonate, gave an end point which coincided with the disappearance of the purple color. Furthermore, the titer decreased as a function of time; this agreed with the disappearance of the oxidized form.

The titration curves for these systems did not agree with the curve for a two-electron system. Fieser observed this and ascribed the deviation to the formation of meriquinone. The deviation found by the present writer was less than that observed by Fieser. The meriquinone formation will have no effect upon the measurements of potential at half oxidation unless the meriquinone is formed with other than a one-to-one ratio of oxidized and reduced forms.

The effect of the introduction of the sulfonic acid grouping was to shift all ionizations of the compound, so that it was now both a weaker acid and a weaker base. This shift occurred with an increase in the oxidation-reduction potential at any given pH.

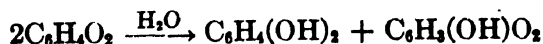
Measurements upon the benzohydroquinone system were undertaken in the hope that measurements in the range in which quinone was unstable might make possible an estimation of the value of the second ionization constant of the reduced form. The potential of the hydroquinone-quinone system should be given by the following expression:

$$E = E_0 - 0.029(?) \log_{10} S_R/S_O + 0.029 \log_{10} (K_1 K_2 + K_1 [H^+] + [H^+]^2)$$

Inspection of this expression, when $S_R = S_O$, shows that the slope for the dependence of the oxidation-reduction potential upon pH should be 0.058 until the pK of the first ionization is reached, at which point the slope should become 0.029. When the pK of the second ionization is reached, the slope should become zero. Examination of the graph of the experimental data in figure 3 shows that the change at the pK of the first ionization occurs, but that at about the point where the pK of the second ionization should be, there is a change in slope back to the original 0.058. Furthermore, the slope between pH 9.8 and pH 12.3 is not the theoretical 0.029 but is 0.0261. This irregular slope indicates that in this region the potential is being determined by a mixture of two systems. At pH 12.3 the benzohydroquinone system must entirely disappear as far as any effect upon the potentials is concerned, for this change in slope would indicate that a group, common to both forms of the system, had now ionized in the oxidized form.

The disappearance of the quinone in the range of pH above 10 was accompanied by the formation of a deep orange-red coloration which faded more or less rapidly, depending upon the pH value, to a yellow. The drift of potentials was rapid, and above pH 11.5 more consistent results were obtained by extrapolating a graph of the antilogarithm of the potential as a function of time. This arbitrary extrapolation agreed closely with the best extrapolation that could be made from the graphs of potential as a function of time. Measurements in this region were made both by adding a ferricyanide solution to a hydroquinone solution and by adding a saturated aqueous solution of quinhydrone to the buffer.

The only system which it appeared might exist, even temporarily, in this region and which might show this behavior was the hydroxyhydroquinone system. The dismutation of quinone is said to occur in the following manner (2, 9, 12):



This reaction may then be followed by (11):



Hydroxyhydroquinone in equilibrium with hydroxyquinone might thus exist in the reaction mixture, although not necessarily in an equimolar mixture. Since this system is formed without participation of hydroquinone, an experiment was run in which a quinone solution was added to the buffer instead of a quinhydrone solution. The value of potential for this experiment (cf. table 3) checked perfectly with those obtained with quinhydrone, and the same color sequence appeared in the solution.

A measured quantity of acidified benzoquinone solution was reduced with hydrogen and colloidal palladium at pH 0.5 and titrated with potassium molybdicyanide solution in an inert atmosphere. The same quantity of quinone solution was then added to 0.1 *M* sodium hydroxide in an atmosphere of nitrogen, and after 30 min. the solution was acidified with sulfuric acid to a pH of 0.5 and titrated with molybdicyanide solution. The titration indicated that 9.2 per cent of a compound 0.100 volt more negative in oxidation-reduction potential than the benzohydroquinone system, and 67.7 per cent of hydroquinone had been formed from the quinone upon dismutation in alkaline solution.

TABLE 6
Constants determined for the two systems

CONSTANTS	BENZOHYDROQUINONE		HYDROXYHYDROQUINONE	
E_0	0.7049 volt	0.7029 volt (1)	0.6014 volt	0.5960 volt (3)
K_1	1.46×10^{-10}	1.33×10^{-10} (4)		
		1.75×10^{-10} (14)		
K_0			10×10^{-4}	.

Measurements upon the hydroxyhydroquinone system were carried out, but in this case, also, the limiting factor was the stability of the quinone. The measurements shown in figure 3 indicate that a group in the oxidized form has a *pK* of approximately 4.0, for above this pH value the slope has changed from 0.058 to 0.087. Above this pH value the solution is orange-red in color, and below it, it is yellow. The quinone was not found to be stable in any solution used. As the solutions were made more and more alkaline, the dismutation of the quinone became more rapid, until above pH 7 the potential-time curves could not be extrapolated to zero time. The potentials showed an initial rise which was very rapid and which indicated formation of the hydroquinone from the quinone.

The constants determined for the two systems are given in table 6. No great significance is to be attached to the discrepancy in the value of E_0 for the benzohydroquinone system, for extreme precision was not being sought in this case. The chief interest in the investigation lay in the alkaline solutions.

Thus it appears from these investigations that the method introduced

by Fieser is capable of extension and application to a great many organic systems ordinarily regarded as irreversible. The greatest success will be obtained with systems which do not give rise to the reduced form of an oxidation-reduction system upon decomposition of the oxidized form.

SUMMARY

1. The oxidation-reduction potentials of the systems arising from *p*-methylaminophenol and from its monosulfonic acid have been measured over a wide range of pH by the discontinuous titration method of Fieser.

2. Measurements have been attempted upon the benzoquinone system in alkaline solution and upon the hydroxyhydroquinone system, but such measurements were hampered by the production of the hydroquinones upon dismutation of the unstable quinones.

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CHEMICAL ACTION OF ALPHA PARTICLES FROM RADON ON AQUEOUS SOLUTIONS¹

F. C. LANNING AND S. C. LIND

School of Chemistry, University of Minnesota, Minneapolis, Minnesota

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INTRODUCTION

The action of radon on aqueous solutions has been relatively neglected. Theoretically, since alpha particles have no selective effect on the separate components of a mixture, one would expect that in dilute or moderately concentrated solutions the principal chemical effect would be exerted upon the solvent water.

It is well known that alpha particles decompose water into hydrogen and oxygen and form a little hydrogen peroxide. If a reducing agent such as hydrogen iodide be present in solution, the evolution of oxygen is suppressed and the equivalent amount of hydrogen iodide is oxidized to free iodine, hydrogen being liberated as gas. The converse case of the acceptance of hydrogen by an oxidizing agent present in solution with liberation of free oxygen has not been previously investigated, but is now demonstrated and quantitatively studied for aqueous solutions of iodine and of potassium permanganate.

Besides the theoretical interest pertaining to such reactions as just described, there is the practical problem of finding a convenient method of calibrating alpha-ray bulbs containing radon. By calibration is meant ascertaining how much ionization will be produced outside such a thin bulb per millicurie of radon contained. Various means of calculation or measurement have been employed. The calculation must assume the bulb to be a sphere of uniform wall thickness. Mund recently devised a very elegant method of making this calculation, but the present experiments show that the assumption of uniform wall thickness is sometimes so far from the truth as to render the application uncertain.

Evidently if one has a solution readily acted on by alpha particles to give a reaction of known yield per ion pair (M/N), it would only be necessary to dip the bulb containing radon into the solution for a suitable interval, titrate the amount of change, and calculate N .

It may be said at the outset that no solution was found capable of

¹ Submitted by F. C. Lanning to the Graduate School of the University of Minnesota in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

yielding a result so simply. Complications, such as reverse reaction, made it necessary to measure the evolved gases also. This complicated the manipulation so that it was found simpler to calibrate the bulb in a separate experiment. A new method² was employed in decomposing gaseous ammonia and measuring the hydrogen and nitrogen left on freezing out the ammonia, which was used in such large excess that the back reaction was negligible.

Besides the employment of alpha-ray bulbs, the radon was also sometimes introduced directly into the water or the solution. As is well known, this method involves a knowledge of the distribution of radon between the liquid and gas phases and also the calculation of recombination of hydrogen and oxygen in the gas phase due to the radon then present. In this connection, it was found that when the neck separating the liquid and gas is narrow (so as to give a sharp demarcation of volumes), the distribution of radon according to the static distribution coefficient cannot be assumed. Apparently the evolved hydrogen and oxygen are carrying radon out through the neck faster than it can redissolve at the small surface, so that the equilibrium is displaced toward excess of radon in the gas phase, calling for a greater correction for back reaction, hence a high yield of the decomposition.

QUALITATIVE RESULTS

Aside from the decomposition of water brought about by radioactive salts dissolved in water, little has been done in the field of radiation of liquids. It is, of course, well known that the radiations produced by a radioactive salt dissolved in water produce decomposition of the water, yielding oxygen, an excess of hydrogen, and a small amount of hydrogen peroxide. In 1907 Cameron and Ramsay (2) studied the decomposition of water brought about by the radiation from radon dissolved in water. Their results indicate that the primary products of decomposition are hydrogen and oxygen in equal quantities and that a secondary reaction ensues with the formation of a small amount of hydrogen peroxide, so that the gas evolved contains a slight excess of hydrogen. They showed that the volume of gas produced was proportional to the amount of radon present in the water, also that the reaction was half completed in 3.8 days, which is approximately the half-life of radon.

Duane and Scheuer (3) showed that the hydrogen excess, amounting to as high as 36 per cent in the initial stage of the radiation, diminished steadily as the experiment proceeded. At very low temperature (183°C.) no excess hydrogen was formed. They concluded that the formation of hydrogen peroxide, and consequent hydrogen excess, was the result of the

² Kindly suggested by Dr. J. C. Jungers.

reaction of nascent oxygen on water. Their calculated values of $-M/N$, the number of molecules of water decomposed per ion pair formed, were between 0.86 and 1.05. Kernbaum (6) measured the amount of hydrogen peroxide formed in radon water solution and showed it to be equivalent to the hydrogen excess. He further showed that the diminishing hydrogen excess was due to establishment of equilibrium in the formation and decomposition of hydrogen peroxide. Lind (7) found that the rate of decomposition of potassium iodide in water, decomposed by means of radon dissolved in the solution, increased with the concentration. Potassium iodide in 2 normal sulfuric acid was decomposed still more rapidly. Nurnberger (9), by a direct method, found $-M/N$ for water to be between 0.7 and 0.9. $-M/N$ for the oxidation of ferrous sulfate, determined by both direct and indirect methods, increased with the concentration, but at higher concentration the $-M/N$ values (approximately 8) are too great to be accounted for by the action of liberated oxygen on ferrous sulfate to form ferric sulfate.

Qualitative experiments were conducted on aqueous solutions of hydrogen iodide, hydrogen bromide, iodine, and iodine in potassium iodide to determine their suitability for quantitative study, the first two as oxygen acceptors, the last two as hydrogen acceptors. The iodine solutions were studied to ascertain if hydrogen is accepted (resulting in synthesis of hydrogen iodide), since this would have an important bearing on the hydrogen iodide decomposition reaction. A 0.5 normal solution of hydrogen iodide in water was exposed to the radiations from radon confined in an alpha-ray bulb mounted on the ground-glass stopper so that it could be introduced into the liquid. Air above the solution was displaced by means of nitrogen. During the course of the reaction the solution was shaken greatly to dislodge any gas bubbles from the alpha ray and also to prevent the accumulation of decomposition products immediately next to the ionization source. After the lapse of a suitable interval of time the alpha-ray bulb was removed, and the solution was titrated with sodium thiosulfate.

By an arrangement similar to that given above for the decomposition of hydrogen iodide, it was shown that iodine, in aqueous solution, accepts hydrogen and is converted into hydrogen iodide. The following data were obtained:

Millicuries.....	140
Time of radiation, in hours.....	22
Ml. of 0.0241 <i>N</i> sodium thiosulfate.....	1.9
Ml. of 0.0335 <i>N</i> barium hydroxide.....	0.75
125 ml. of 0.00108 <i>N</i> iodine = 5.6 ml. of 0.0241 <i>N</i> sodium thiosulfate	

Calculations:

(1) From the sodium thiosulfate titration:

$$\frac{5.6 - 2(1.9)0.024 \times 127.94}{1000} = 0.0055 \text{ g. of hydrogen iodide}$$

(2) From the barium hydroxide titration:

$$\frac{2 \times 0.75 \times 0.0335 \times 127.94}{1000} = 0.0064 \text{ g. of hydrogen iodide}$$

These results (although they do not agree exactly) indicate that there is at least some reaction between hydrogen from the primary decomposition of water and iodine in neutral solution with the formation of an equivalent amount of hydrogen iodide.

This experiment was next repeated with iodine in potassium iodide, to ascertain if iodine will combine to form hydrogen iodide. The results from four experiments showed no loss of iodine and no formation of hydrogen iodide. It was therefore concluded that there should be no back reaction in the decomposition of hydrogen iodide, since the iodine would, in all probability, exist in combination with hydrogen iodide as HI_3 , as it does with potassium iodide as KI_3 . Hydrogen iodide would, therefore, appear suitable for more extended study as oxygen acceptor. It should be noted that, in the results to be reported later in this reaction, the hydrogen iodide is 0.5 *N* (more than twice as concentrated as the potassium iodide in these preliminary experiments), and, further, that the iodine formed is always much less concentrated than the iodine used in the potassium iodide solutions.

QUANTITATIVE RESULTS

1. *Decomposition of water and aqueous hydrobromic acid solutions by the direct method*

The reactions were carried out in the apparatus shown in figure 1. B is the reaction vessel containing the solution. It is connected to the vessel *a* by means of a capillary tube of 3-mm. diameter. The volume of B = 56.0 cm.³ The vessel *a* during the experiment will contain evolved gases and radon in equilibrium with the radon in the solution. The vessel carries sealed-in tungsten electrodes for sparking evolved gases. The volume of the vessel, together with connecting capillary tubes to the manometer, is 4.29 cm.³ The liquid in B can be agitated by means of a glass-covered bead of soft iron actuated by an electromagnet. The procedure followed was to introduce the radon into the evacuated vessels, A and B, by means of the special device, D, which consists of a metal rod with an eye at the top through which the radon capsule was inserted. By turning the metal cup to which the rod is attached the capsule may be

broken, allowing the radon to diffuse up into the reaction vessel, from G, through the connecting tubes and E. The course of the reaction was followed manometrically, by taking pressure readings at suitable intervals, both before and after sparking the evolved gases in the vessel A.

At the conclusion of the hydrogen bromide experiments, the liquid was withdrawn and analyzed for liberated bromine. Potassium iodide was added to the hydrogen bromide solution, and the liberated iodine was

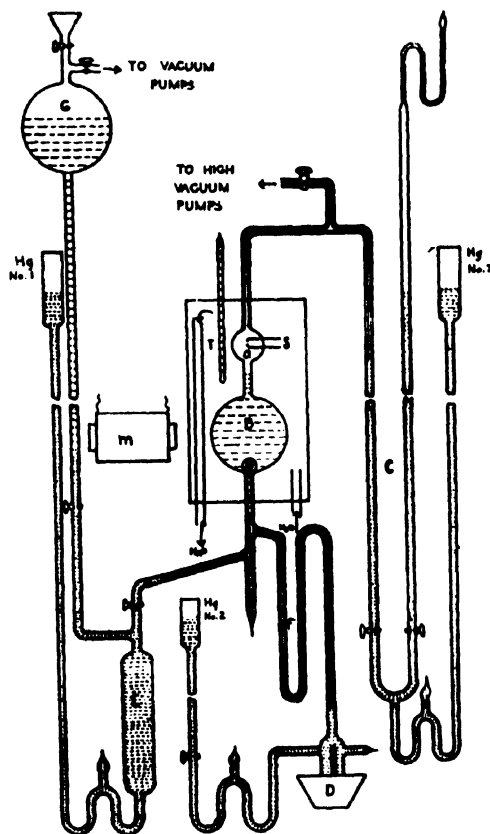


FIG. 1. Apparatus for the direct radiation of water and hydrobromic acid

titrated with standard sodium thiosulfate solution. Calculations for both water and hydrogen bromide were made on the manometric data obtained.

Before calculations could be made it was necessary to determine the distribution of radon between the liquid and gas phases. The conditions under which these experiments were performed made it impossible to use the distribution coefficient of St. Meyer and Schweidler. In order to define the gas volume with sufficient accuracy to make possible suitable

manometric measurements on the hydrogen and oxygen evolved, a small-bore tube, connecting vessels A and B, had to be used. The evolution of the hydrogen and oxygen in the liquid, and diffusion into the vessel above,

TABLE 1

Direct method for decomposition of water by radon

Experiment I: initial quantity of radon = 86.7 mc.; $T = 13^\circ\text{C}$.

TIME	P_1^*	P_2	V	M_1	M_2	N
hours	cm.	cm.				
9.5	3.52	0.71	0.249			
18.5	8.97	1.39	0.635			
25	12.89	2.22	0.912			
35	17.35	3.56	1.23			
45.5	22.34	5.2	1.58	0.95	0.093	1.69
59	27.79	7.25	1.97	1.95	0.212	3.78
70	32.53	8.88	2.30	2.84	0.299	5.23
82.5	36.46	10.35	2.58	3.60	0.389	6.17
90.5	39.07	11.34	2.805	4.20	0.442	7.03
105	43.02	12.85	3.085	4.97	0.534	8.08
117	47.14	14.58	3.388	5.79	0.610	9.10
130.5	50.45	16.07	3.62	6.40	0.687	10.06
139.5	51.80	16.50	3.725	6.69	0.737	10.68
161.5	57.60	18.86	4.13	7.80	0.853	12.38
185.5	62.32	20.97	4.47	8.70	0.956	13.48

PER CENT DISTRIBUTION OF RADON			$M = 8.70 \times 10^{19} + 0.956 \times 10^{19}$ $M = 9.656 \times 10^{19}$ $-\frac{M}{N}(\text{H}_2\text{O}) = \frac{9.656 \times 10^{19}}{13.48 \times 10^{19}} = 0.716$
Hours	Rw	Rg	
36	40.7	59.3	
61.5	40.8	59.2	
106.0	38.6	61.4	

* P_1 = total pressure of hydrogen produced, in centimeters.

P_2 = total pressure of oxygen produced, in centimeters.

V = volume at standard conditions of hydrogen produced.

$M_1 \times 10^{19}$ = molecules of hydrogen in V .

$M_2 \times 10^{19}$ = molecules of water resynthesized.

$M \times 10^{19}$ = molecules of water decomposed = $M_1 + M_2$.

$N \times 10^{19}$ = number of ion pairs produced in water.

T = average temperature.

Volume of liquid in each case = 56.0 cc.

Rw = per cent of radon in the liquid phase.

Rg = per cent of radon in the gas phase.

not only prevented the prompt establishment of equilibrium of the radon between the gas and liquid phases, but also displaced the equilibrium toward the gas phase. This necessitated making actual measurements of radon distribution throughout the course of the experiment. This was

done by x-ray comparison, using a Lind electroscope with heavy lead shielding first between A, then B, and the electroscope.

The data on the water and hydrobromic acid experiments are given in tables 1 and 2.

TABLE 2
Direct method for decomposition of hydrobromic acid by radon
Experiment III: radon in 0.397 *N* hydrobromic acid

hours	P_1^* cm.	P_2 cm.	V	M_1	M_2	N
15	5.53	1.367	0.388	1.048	0.221	3.185
29	16.45	1.473	1.152	3.12	0.121	6.885
40	25.58	1.867	1.792	1.73	0.120	2.86
51	35.15	2.147	2.46	3.53	0.247	5.56
63	44.85	2.367	3.14	5.37	0.419	8.51
75	54.41	2.63	3.815	7.20	0.587	11.04
89	63.04	2.95	4.42	8.85	0.783	13.47

DISTRIBUTION OF RADON

Hours	R_w	R_g
16	41.2	55.8
69.5	50.2	49.8
88	48.9	51.1

$$M = 8.85 \times 10^{19} + 0.783 \times 10^{19}$$

$$M = 9.633 \times 10^{19}$$

$$\frac{M_{H_2}}{N_{H_2O}} = \frac{9.633 \times 10^{19}}{1.347 \times 10^{19}} = 0.716$$

	$-M_{HBr}/N_{H_2O}$
A. From titration of bromine liberated.....	1.155
B. From hydrogen liberated.....	1.187

$$\text{Per cent oxygen utilized} = \frac{1.155 \times 100}{2 \times 0.716} = 80.5.$$

* See footnote to table 1.

Calculations of M_{H_2}/N_{H_2O} :

$$M_{H_2} = M_1 + M_2$$

M_1 is the number of molecules of hydrogen produced as determined by the gas measurements. M_2 is the number of molecules of hydrogen resynthesized in the gas phase.

$$M_1 = \frac{V \times \text{Avogadro's number}}{22,400}$$

V is the volume (under standard conditions) of hydrogen produced.

$$M_2 = 5.34 \times 10^{13} \times 2.4 \times 10^4 \times mc_i \times \bar{P} \times i \times \frac{P}{760} \times Y \times 3.85$$

In this expression $mc.$ is the number of millicuries of radon decayed in the gas phase, \bar{P} is the average path, in centimeters, that an alpha particle would travel, P is the average pressure, in millimeters, over the period calculated, i is the specific molecular ionization of the gas mixture referred to air as unity, Y is a factor to take into account the ionization produced by recoil atoms, and 3.85 represents the number of molecules of water produced per ion pair. \bar{P} is equal to 0.61 times the radius of the sphere. The term i is calculated using the average pressures of hydrogen and oxygen during the period. Y is given by the expression $\frac{R + \alpha}{\alpha}$, in which R represents the ionization produced by recoil atoms and α the ionization produced by alpha particles.

The ionization N_{H_2O} is given by the following expression, in which α is the number of alpha particles per millicurie disintegrated, $mc.$ is the number of millicuries of radon destroyed in the liquid, P_1 is the number of ion pairs produced per alpha particle, and KS is the molecular ionization of water (0.82).

$$N_{H_2O} = \alpha \times mc. \times P_1 \times KS$$

Calculation of $-M_{HBr}/N_{H_2O}$:

(1) from gas measurements: To obtain $-M_{HBr}$ from the gas measurements, it is necessary to correct only $M_1(H_2)$ for the unused oxygen and multiply by 2.

$$-M_{HBr} = 2 \left[M_1 - \left(\frac{M_1 \times 2 \times \text{total cm. pressure of oxygen produced}}{\text{Total cm. pressure of hydrogen produced}} \right) \right]$$

(2) from titration: The titration was 23.1 cm.³ of 0.01483 N sodium thio-sulfate.

$$-M_{HBr} = \frac{23.1 \times 0.01483 \times 6.06 \times 10^{23}}{1000} = 20.8 \times 10^{19}$$

$$N_{H_2O} = 18.01 \times 10^{19}$$

$$\frac{-M_{HBr}}{N_{H_2O}} = \frac{20.8 \times 10^{19}}{18.01 \times 10^{19}} = 1.155$$

Owing to the difficulties encountered in the measurements of distribution of radon between the liquid and the gas and in the calculation of the amount of recombination of the gases under the influence of the radon mixed with them, this direct method proved to be unsatisfactory. Since the use of an alpha-ray bulb eliminates both of these problems, the remainder of the work here reported was done by this indirect method. As will be pointed out later, it does require a careful calibration of the alpha-ray bulb.

ter, wall thickness, and tip and stem corrections. Our investigation of the thickness of the walls of many alpha-ray bulbs, both by microscope and the interferometer, convinced us that the assumption of uniformity of wall thickness is not justified, and that the bulb must be calibrated by using it as an ionization source in a reaction whose ion yield is accurately known. The ammonia decomposition, suggested by Jungers, lends itself readily for this standardization. The apparatus used, together with that used for the potassium permanganate reduction, is shown in figure 2. The

TABLE 3

Determination of $-M/N$ for water with a bulb standardized against ammonia decomposition

Initial quantity of radon = 125.9 mc.; $T = 22^\circ\text{C}.$; h_1 (zero manometer reading) = 600;
 P_1 (pressure of ammonia) = 1.36 atm.

EXPERIMENT NO.	TIME ELAPSED FROM START	DURATION OF EACH EXPERIMENT	h MANOMETER READING	P PRESSURE OF GASES PRODUCED	mc. RADON DESTROYED IN EACH EXPERIMENT	P/mc.	-M/N
Standardization against ammonia							
1	10	10	645.0	45.0	9.09	4.95	0.868*
2	12 } 27 }	15	659.5	59.5	12.25	4.87	0.880
3	30 } 47.5 }	17.5	662.0	62.0	12.42	4.98	0.862
							Av. = 0.870
Radiation of water							
4	130 } 191 }	61	649	49	17.3	4.18	
After sparking			630	30			

* Calculations: (1) $(4.18 \times 1.023)/4.95 = 0.868$; (2) $(4.18 \times 1.023)/4.87 = 0.880$; (3) $(4.18 \times 1.023)/4.98 = 0.862$.

reaction vessel, A, in the center of which the alpha-ray bulb is suspended, is of sufficiently large diameter to insure complete absorption of all α -particles by the ammonia at the pressures used. At intervals the ammonia is frozen down in C and the gases, nitrogen and hydrogen, are pumped out and measured.

The vessel, H, is a Dewar flask to which the small bulb, I, is attached. A side tube on I makes it possible to seal in the glass rod carrying the alpha-ray bulb which has been calibrated by the method just described. The whole is then sealed on to the Toepler pump and measuring apparatus at X.

In table 3 are given the data on three experiments on ammonia decomposition and one on water, all using the alpha-ray bulb containing, initially, 125.9 mc. of radon. The calculation of $-M/N$ for water, using a bulb calibrated in this manner, is as follows: Inspection of the decomposition equations



shows that the total volume of gas evolved in reaction 1 is twice that of the hydrogen only, in reaction 2, per molecule decomposed. Comparison is made on this basis because of the fact that hydrogen is always in slight excess and more accurately represents the total reaction than the volume of oxygen or the mixture of hydrogen and oxygen. It happens that the molecular ionization of ammonia and that of water are the same, so that this factor (Bragg's *KS*) need not be taken.

Calculation

30 - 19.63 (V.P.) = 10.37 mm. of excess hydrogen

49 - 10.37 = pressure of the electrolytic mixture

2/3 (49 - 10.37) = 25.8 mm., pressure of hydrogen in the electrolytic mixture

25.8 + 10.37 = 36.17 mm., total hydrogen

36.17 \times 2 = 72.34 mm., total pressure of hydrogen and nitrogen which would have been formed

17.3 mc. of radon decayed during the interval

$$\frac{72.34}{17.3} = 4.18 \text{ mm. per millicurie}$$

This value from the ammonia decomposition using the same bulb is 45.0/9.09 = 4.95. Thus 4.95:4.18 = 1.023:X, in which 1.023 is the value adopted, from the work of Jungers (5), for $-M/N$ for ammonia and X is the value of $-M/N$ for water. Thus $-M/N$ for water = 0.868. This value agrees well with those between 0.86 and 1.05, which were obtained by Duane and Scheuer (3).

Again, it should be pointed out that some resynthesis of water occurs within the bubbles clinging to the alpha-ray bulb, and, while it is impossible to estimate with any degree of accuracy the magnitude of the error which this introduces, it is safe to conclude that the true value of $-M/N$ for the decomposition of liquid water is very close to unity and that at least the net reaction is the decomposition of one molecule of water into hydrogen and nascent oxygen per ion pair.

In the two reactions now to be described, the alpha-ray bulbs used were calibrated by the water decomposition, measuring the volume of hydrogen evolved, assuming the value of $-M/N$ for water to be 0.87.

3. Decomposition of hydrogen iodide

In the preliminary studies it was shown that hydrogen iodide solutions, under the influence of radiations from radon, are decomposed with the liberation of iodine and hydrogen. The iodine may be conveniently titrated, and the hydrogen is readily measured manometrically. It was further shown that there is very probably no back reaction under the conditions of the experiments here reported. All the iodine formed has a high probability of forming I_3^- , which was proved to be stable under alpha radiation. The apparatus and method are essentially the same as that

TABLE 4

Determination of $-M_{HI}/N_{H_2O}$ with a bulb standardized against water

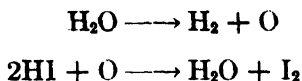
Experiment I: initial quantity of radon = 88 mc.; $T = 32^\circ\text{C}$.

TIME ELAPSED FROM START	DURATION OF EACH EXPERIMENT	P_1 PRESSURE BEFORE SPARKING	P_2 PRESSURE AFTER SPARKING	P_{H_2} TOTAL PRES- SURE OF HYDROGEN PRODUCED	mc. RADON DESTROYED	$P/\text{mc.}$
Standardization against water						
hours	hours	mm.	mm.	mm.	mc.	mm.
14	14	17.7	15.8			
24.5	24.5	35.85	26.35			
38	38	42.5	31.6			
50	50	56.7	40.45	69.04	27.3	2.53
Radiation of 0.5 N hydrogen iodide solution						
62	0					
96.5	34.5	38.05	38.05	41.09	14.97	2.74
						$-M_{HI}/N_{H_2O}$
From gas measurements $\left(\frac{2 \times 2.74 \times 0.87}{2.53}\right)$						1.88
From titration (5.0 - 0.2 = 4.8 ml. of 0.01538 N sodium thiosulfate)						1.87

described for the hydrogen bromide decomposition, except that the radon is confined in an alpha-ray bulb located in the center of the reaction vessel; and thus no measurements on the distribution of radon are necessary. The alpha-ray bulb is calibrated against water, using the $-M/N$ value (for water) previously found by standardization against ammonia. The results are given in table 4.

As will be seen in table 4, there was no loss of pressure on sparking the gases. This indicates that all of the oxygen evolved for the primary decomposition of water is utilized in decomposing hydrogen iodide. The table also shows that the calculated $-M_{HI}/N_{H_2O}$ values from the hydrogen

pressure measurements and for the titration of liberated iodine, respectively, agree closely. Note that this agreement is quite independent of the calibration against water also reported in table 4. The absolute value of $-M_{\text{HI}}/N_{\text{H}_2\text{O}}$ (1.88) does, of course, depend on this calibration and should, as indicated in the calculations given herewith, be twice that for $-M/N$ (H_2O). (This value for the ammonia decomposition comparison is 0.87.) That is, the value should be 1.74 if the theory of secondary utilization of oxygen is correct as indicated in the equations:



The fact that it is somewhat higher is probably brought about because there is less recombination of hydrogen and oxygen in the gas bubbles formed on the alpha-ray bulb, since the oxygen is so promptly absorbed by hydrogen iodide, although there is undoubtedly some recombination in the bubbles even here. (Any oxygen actually in a bubble as it breaks away from the surface of the alpha-ray bulb is apparently completely absorbed before it escapes from the liquid.) It seems altogether probable, therefore, that the true values are:

$$\frac{-M}{N} \text{ (for } \text{H}_2\text{O}) = 1 \quad \text{and} \quad \frac{-M_{\text{HI}}}{N_{\text{H}_2\text{O}}} = 2$$

4. Determination of $-M_{\text{KMnO}_4}/N_{\text{H}_2\text{O}}$

The apparatus is the same as that used for ammonia and pure water, and is shown in figure 2, H and I being sealed on at X, as described previously. The potassium permanganate solution to be radiated is made by pipetting the desired quantity of a stock solution of aqueous potassium permanganate into water and adding the desired amount of aqueous c.p. sulfuric acid. The water used is conductivity water. A sample identical with that radiated is stored under vacuum until the end of the experiment and is then titrated in the same way as the radiated sample.

The procedure is to radiate a solution of potassium permanganate by means of an alpha-ray bulb (calibrated against water in the same apparatus). The evolved gases are measured before and after sparking. The solution is withdrawn and potassium iodide added, after which it is titrated with sodium thiosulfate. Results are shown in tables 5, 6, and 7. The calculation of $-M_{\text{KMnO}_4}/N_{\text{H}_2\text{O}}$ from the data given in table 5, having to do with the radiation of potassium permanganate, will now be given. The number of molecules of potassium permanganate which have been reduced is given by the following equation

$$-N_{\text{KMnO}_4} = \frac{5.85 \times 0.01426 \times 6.06 \times 10^{23} \times 0.9377}{5 \times 1000} = 0.945 \times 10^{19}$$

TABLE 5

*Determination of $-M_{\text{KMnO}_4}/N_{\text{H}_2\text{O}}$ with a bulb standardized against water*Experiment I: initial quantity of radon = 89.3 mc.; $T = 26^\circ\text{C}$.

TIME ELAPSED FROM START	DURATION OF EACH EXPERIMENT	P_1 PRESSURE BEFORE SPARKING	P_2 PRESSURE AFTER SPARKING	P_{O_2} PRESSURE OF OXYGEN PRODUCED	mc. RADON DESTROYED	$P_{\text{O}_2}/\text{mc.}$ PRESSURE OF OXYGEN PRODUCED PER MILLICURIE OF RADON DESTROYED
Standardization against water						
hours 30	hours 30	mm. 38	mm. 25.81	mm. 12.81	mc. 18.3	mm. 0.712
Radiation of 0.3 N potassium permanganate solution, normal in sulfuric acid						
48 149.5	0 101.5	71	68	62	33.1	1.875

TABLE 6

*Determination of $-M_{\text{KMnO}_4}/N_{\text{H}_2\text{O}}$ with a bulb standardized against water*Experiments II and III: initial quantity of radon = 134.3 mc.; $T = 23^\circ\text{C}$.

TIME ELAPSED FROM START	DURATION OF EACH EXPERIMENT	P_1 PRESSURE BEFORE SPARKING	P_2 PRESSURE AFTER SPARKING	P_{O_2} PRESSURE OF OXYGEN PRODUCED	mc. RADON DESTROYED	$I_{\text{O}_2}/\text{mc.}$	DIFFERENCE IN PERMANGANATE TITRATIONS
Standardization against water							
hours 22	hours 22	mm. 56.8	mm. 31.9	mm. 19.12	mc. 20.45	mm. 0.934	
Radiation of 0.0848 N potassium permanganate, 1.25 N in sulfuric acid							
26 43	0 17	49.0	40.0	20.3	14.08	1.44	5.85 ml. of 0.01426 N sodium thiosulfate
Radiation of 0.371 N potassium permanganate, 1.25 N in sulfuric acid							
72 98	0 26	43.0	41.33	34.7	13.9	2.49	9 ml. of 0.01426 N sodium thiosulfate

TABLE 7

The values of $-M_{\text{KMnO}_4}/N_{\text{H}_2\text{O}}$ obtained from the radiation of aqueous solutions of potassium permanganate containing sulfuric acid

KMnO ₄	H ₂ SO ₄	$-M/N$ FROM TITRATION	$-M/N$ FROM GAS
N	N		
0.0848	1.25	0.516	0.536
0.3	1.0		0.907
0.37	1.27	0.864	0.922

in which 5.85 is the difference in volume of 0.01426 *N* sodium thiosulfate solution required by the unirradiated and radiated solutions. 0.9377 is a correction term to take account of the time elapsing while the apparatus is being assembled, evacuated, etc. During this time the potassium permanganate is being acted upon, but the collection of gases cannot be started. The number of molecules of water decomposed in the water standardization is given by the following equation:

$$-M_{\text{H}_2\text{O}} = \frac{19.12 \times 17 \times 2 \times 6.06 \times 10^{23}}{760 \times 22,400} = 2.31 \times 10^{19}$$

Using the value $-M_{\text{H}_2\text{O}}/N_{\text{H}_2\text{O}} = 0.87$, found above by ammonia standardization,

$$N = \frac{2.31 \times 10^{19}}{0.87} = 2.65 \times 10^{19}$$

The number of millicuries of radon decayed for the production of this number of ion pairs was 20.45. For the 17-hr. interval during which potassium permanganate was being radiated, 14.08 mc. of radon decayed. Consequently, the corresponding number of ion pairs produced was

$$2.65 \times 10^{19} \times \frac{14.08}{20.45} = 1.83 \times 10^{19}.$$

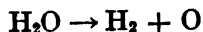
Therefore,

$$\frac{-M_{\text{KMnO}_4}}{N_{\text{H}_2\text{O}}} = \frac{0.945 \times 10^{19}}{1.83 \times 10^{19}} = 0.516$$

$-M/N$ values for the other concentrations of potassium permanganate calculated in the same way are shown in table 7.

Discussion of potassium permanganate reaction

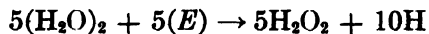
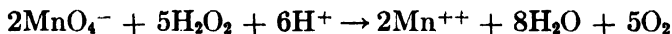
As will be seen, the value of $-M/N$ increases with the concentration. For the more concentrated solutions the value is approximately that found for water. If our previous conclusion that the true value for water is unity is correct, that should also be the value for $-M_{\text{KMnO}_4}/N_{\text{H}_2\text{O}}$ in the more concentrated solutions. This is 2.5 times as large as can be accounted for on the assumption that the entire primary reaction is



and that potassium permanganate is reduced solely by hydrogen



It is obvious that some other reaction occurs which results in the reduction of potassium permanganate. The following series of equations accounts for the results in a fairly satisfactory manner:

1. *Primary reaction:*2. *Secondary reactions:*

Thus there should be 0.8 as many potassium permanganate molecules decomposed as water molecules, by the primary reaction. In other words, $-M/N$ for potassium permanganate should be 0.8 of the value of $-M/N$ for water. Our experiments are not as close as desirable for upholding the theory, but are, nevertheless, within reason.

The low results for the more dilute solutions can be explained by less utilization of the hydrogen. The more dilute the solution, the less the probability of the hydrogen being used before it reaches the gas phase. This conclusion is justified by the results, as the excess hydrogen was larger in the case of the dilute solutions.

The assumption that the primary decomposition of water into hydrogen peroxide is made here, since it seems unlikely that if the decomposition were into hydrogen and oxygen, the oxygen would react quantitatively with water to form hydrogen peroxide, as would be necessary to explain the results. Further evidence for this conclusion is given in the section on mechanisms.

5. *Mechanisms*

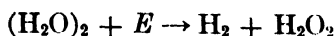
Until the permanganate solutions were studied, all the effects produced in solution could be explained by the classical theory that water is decomposed directly into hydrogen and oxygen on being radiated by alpha particles. This theory is based on some results of Duane and Scheuer (3). They concluded that hydrogen peroxide was formed by the secondary reaction of nascent oxygen on water, and they based their conclusion on the experimental fact observed by them that the gases liberated at -183°C . under alpha radiation consisted wholly of electrolytic gas.

More recent work by Bonhoeffer and Reichardt (1) adds new light to this question and undermines the classical theory. They radiated water vapor at a temperature of 1000° to 1600°C . with ultraviolet light and obtained spectra for free hydroxyl. With this evidence, along with further considerations, they concluded that the mechanism for the decomposition of water under these conditions is given by the following equation:

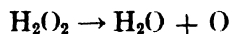


Two free hydroxyl groups obviously correspond to a dissociated hydrogen peroxide molecule. This leads to the conclusion that the decomposi-

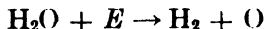
tion of water in the liquid state produced hydrogen and hydrogen peroxide. Water in the liquid state is largely associated into $(\text{H}_2\text{O})_2$ molecules. It is rather difficult to understand how one of the water molecules in the associated molecule could be influenced by the ionization without the other one being influenced, but it is easy to see how the two could be decomposed into hydrogen and hydrogen peroxide. E , in the equations, represents the energy necessary to produce one ion pair.



Considering the evidence of Bonhoeffer and Reichardt (1), the necessity of using this mechanism for explaining the permanganate reaction and the fact that it is a logical one leads one to accept the above equation as being the true mechanism. The adoption of this new mechanism in no way affects the discussions and conclusions made from the classical theory as the net result is the same, since hydrogen peroxide is an unstable intermediate product. Probably some of that formed decomposes almost instantly.

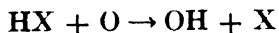


The equation for the net result of water decomposition is then as follows:

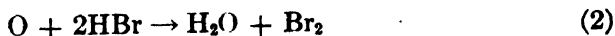
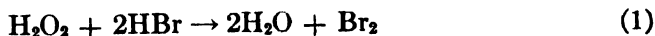


This is the same equation as is obtained by the classical theory.

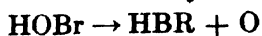
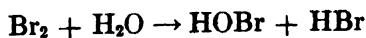
Before considering the mechanisms for the hydrogen bromide and hydrogen iodide decompositions, the work of Harteck and Kopsch (4) on reactions with atomic oxygen should be mentioned. With electrically produced atomic oxygen they obtained spectra showing reactions between the oxygen and halogens.



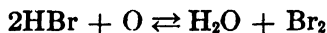
Thus we can conclude that the decomposition of the halogen acids can be due to both hydrogen peroxide and nascent oxygen liberated from the peroxide. The primary reaction, in the case of the hydrobromic acid, must be between it and hydrogen peroxide, and there must also be some reaction between it and nascent oxygen liberated from hydrogen peroxide.



Bromine reacts with water to form hydrobromic acid and hypobromous acid, which is unstable and decomposes to hydrobromic acid and oxygen.

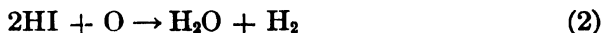
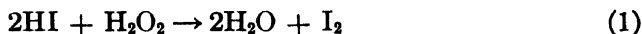


Then an equilibrium is set up, as shown in the following equation:



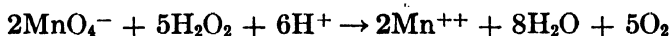
The per cent of oxygen utilized evidently depends on the concentrations and on the equilibrium constant, which depends on the temperature.

In the case of the hydriodic acid decomposition, the reaction goes to completion and the reactions taking place are as follows:



The first reaction is the chief one.

The permanganate decomposition requires two reactions to explain the production of 2.5 atoms of oxygen per permanganate molecule decomposed.



These reactions must also be equally probable to explain the results in the less dilute solutions. Furthermore, the reaction between the hydrogen peroxide and permanganate is assumed to take place before the hydrogen peroxide has a chance to decompose otherwise. The fact that the value of $M_{\text{KMnO}_4}/N_{\text{H}_2\text{O}}$ drops for more dilute solutions is explained by the increased probability of hydrogen escaping from the solution before it takes part in the second reaction.

SUMMARY

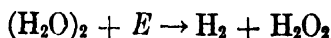
A study has been made of alpha radiation of water and of certain aqueous solutions, with the following results:

1. Hydrogen iodide is decomposed into hydrogen and iodine; hydrogen bromide into hydrogen and bromine.
2. Iodine in pure water is shown to accept hydrogen and form hydrogen iodide.
3. Iodine in potassium iodide solutions is shown not to be a hydrogen acceptor.
4. Potassium permanganate solutions containing sulfuric acid are decomposed. Manganous sulfate is formed.
5. By the direct method, with the radon dissolved in water, the value of $-M/N$ for water was found to be 0.739; for hydrogen bromide, 1.187.
6. By the indirect method, with the radon in an alpha-ray bulb standardized by ammonia decomposition, the value of $-M/N$ for water was found to be 0.87.
7. It is concluded that the true value of $-M/N$ for water = 1. By the indirect method, $-M/N$ for hydrogen iodide = 1.86. If the true value of $-M/N$ for water is 1, the true value of $-M/N$ for hydrogen iodide is 2.

8. By the indirect method — M/N for potassium permanganate is 0.516 in 0.0848 N potassium permanganate and 0.893 in 0.37 N potassium permanganate, each potassium permanganate solution being approximately normal in sulfuric acid.

9. The primary effect is the decomposition of water, and the effects on solutes are produced purely by secondary reactions instigated by the decomposition products of water.

10. The evidence seems to indicate that the primary effect is the decomposition of water into hydrogen peroxide and hydrogen:



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NEW BOOKS

Second Report on Viscosity and Plasticity. Prepared by the Committee for the Study of Viscosity of the Academy of Sciences at Amsterdam. vi + 287 pp. New York: Nordemann Publishing Company, Inc., 1938. Price: \$7.50.

These *Reports on Viscosity and Plasticity* owe their origin to a suggestion of the International Council of Scientific Unions to found a committee for the purpose of "accumulating data on the use of instruments and methods developed in special branches of science, in order to make them known also in other branches." The choice of the problem made by the Dutch Academy appears to be particularly appropriate. Viscosity and plasticity are of paramount importance in many fields of work, for industrial and biological problems no less than for those of physics and chemistry, and our theoretical knowledge is poor. The use of the plastic properties of clay is one of the oldest of man's technical successes; the shards of pottery are the "leading fossil" by which the development of human culture is followed down to very early strata. Nevertheless how very little is known, from the point of theory, about plasticity, compared, for instance, to our knowledge of electrical machines, though the electromagnetic phenomena were discovered not much more than one hundred years ago. And as to viscosity, but recently Andrade first proposed a fairly promising theory correlating the viscosity of liquids with the mass and frequency of thermal vibrations of their molecules.

The first of these reports, published in 1935, contained the following chapters: I. Mechanical Considerations—Model Systems—Phenomenological Theories of Relaxation and Viscosity (by J. M. Burgers); II. Remarks in Connection with the Experimental Investigation of Flow Properties (by J. M. Burgers); III. Viscosity Measurements with Special Reference to their Application in Colloid Chemistry (by H. B. Bungenberg de Jong); IV. Viscosity and Plasticity from a Technical Point of View (by C. J. van Nieuwenburg); V. Plasticity of Crystalline Substances, in Particular of Metals (by W. G. Burgers and J. M. Burgers); VI. Viscosity Effects in the Living Protoplasm and in Muscles (by H. J. Jordan).

The second report contains: I. Introductory Remarks on Recent Investigations concerning the Structure of Liquids (by J. M. Burgers); II. Viscosity of Liquids in Connection with their Chemical and Physical Constitution (by F. M. Jaeger); III. On the Motion of Small Particles of Elongated Form, Suspended in a Viscous Liquid (by J. M. Burgers); IV. The Yield Value (by R. Houwink); V. Recent Plastometers (by C. J. van Nieuwenburg); VI. Technical Capillary Viscometers (by R. N. J. Saal).

The chapters by Burgers, Bungenberg de Jong, and Houwink are particularly suggestive for those interested in physical and colloid chemistry. The chapters of the last two authors cover a part of the viscous and plastic properties of colloidal systems, but not those of gels, which will probably be treated in a later report.

H. FREUNDLICH.

Dipole Moments. Their Measurement and Application in Chemistry. By R. J. W. LE FÉVRE. 10 x 16.5 cm.; 105 pp.; 28 diagrams. New York: Chemical Publishing Company of New York, Inc., 1938. Price: \$1.50.

This little monograph covers the following range of topics: I. Dielectric Polariza-

tion and the Calculation of Dipole Moments; II. Practical Methods for the Measurement of Dipole Moments; III. Solvent Effect in Dipole Moment Measurements; IV. Dipole Moments and Molecular Structure; V. Intramolecular Rotation and Flexibility of Molecules; VI. Some Anomalous Dipole Moments. It contains as well an abridged table of dipole moments.

As is evident from its size, the booklet does not undertake to be complete in detail nor to provide an exhaustive bibliography. It does give a useful condensed account of a subject which, after a dozen or more active years of study, is still attracting a good deal of interest. Particular attention is directed to fundamental theories, experimental methods, and interpretation of dipole moment data. Relations of the results to other fields of investigation are considered. The mathematical apparatus is reduced to a minimum. This clearly written monograph should prove of great interest and utility to those chemists who have found the more ambitious treatises too abstruse for their requirements.

The author deserves praise for the care with which he has done his work. The material is carefully organized and discussions are clear and attractively presented. The general appearance of the text is excellent. Perusal of this book should stimulate a more widespread interest in the subject.

J. W. WILLIAMS.

Mikroanalytische Nachweise anorganischer Ionen. By GERHARD KRAMER. 35 pp.; 8 plates. Leipzig: Akademische Verlagsgesellschaft, 1937. Price: 5.60 RM.

This booklet contains directions for carrying out crystal tests for the common metals and a few of the acid radicals. The reactions described are old classical ones which for the most part have stood the test of time. Some common forms of identification, such as zinc and cadmium mercuric thiocyanates and the "triple acetate" of sodium, are not mentioned. The sensitivity of the reactions is expressed, as is so often done, in terms of the absolute amount of the ion that can be detected in a drop of arbitrary size (in this case 0.03 ml.). It would seem to be better practice to base the expression for the sensitivity on the limiting concentration of the solution tested instead of on an absolute amount which has little real significance.

Forty-eight excellent photomicrographs are included in the work.

E. B. SANDELL.

An Introduction to Microchemical Methods for Senior Students of Chemistry. By CECIL L. WILSON. 196 pp.; 93 diagrams. New York: Chemical Publishing Company of New York, Inc., 1938. Price: \$3.00.

A wide range of topics is included in this little volume. Among others, there are chapters on the compound microscope, the polarizing microscope, crystal tests, spot tests, inorganic qualitative analysis, inorganic gravimetric and volumetric analysis, the colorimeter, the nephelometer, organic operations, organic quantitative analysis, photomicrography, and the spectrograph. The book is hardly suitable for use as a text, because of the limited space that can be allowed so many different phases of the subject. The author himself says "... the work here described is only preliminary, and should be followed by the use of textbooks by recognized authorities in each branch ...". The book serves a distinctly useful purpose in giving a general survey of a vast field, and it contains a surprising amount of information in a small space.

E. B. SANDELL.

Negative Ions. By H. S. W. MASSEY. 105 pp., 19 figs. Cambridge Physical Tracts. Cambridge, England: University Press, 1938. New York: The Macmillan Company, 1938.

This volume contains a very excellent discussion of negatively charged particles

in respect to their occurrence, production, and behavior. The treatment covers both experimental results and theoretical considerations. The latter are carried out along the modern lines of wave mechanics. The book abounds with suggestions for further research and should be of greatest interest to workers in the field. However, all scientific workers, especially physicists and chemists, can readily bring their knowledge of this particular branch of atomic and molecular physics up-to-date by a perusal of this tract. The five chapters cover the following items: negative atomic ions; negative molecular ions; modes of formation of negative ions; detachment of electrons from negative ions; negative ions in the glow discharge and in the upper atmosphere.

GEO. GLOCKLER.

Elementary Survey of Physics. By ARTHUR E. HAAS AND IRA M. FREEMAN. 203 pp.; 75 figs. New York: E. P. Dutton and Company, 1938. Price: \$1.90.

This is a brief survey and compilation of physics which the authors suggest may be used to acquaint students, among them premedical students, with the whole field of physics. Its briefness has led to a number of naïve statements and generalizations, and the reviewer hopes that all premedical students will be required to complete a more comprehensive and detailed course than is given here. The essentials of physics are stated in the book, but it alone would give a very superficial knowledge of the field.

J. W. BUCHTA.

Spectrochemical Abstracts, 1933-1937. By F. TWYMAN. 24 x 15 cm.; 52 pp. London: Adam Hilger, Ltd., 1938. Price: 3/10.

This handy volume contains brief abstracts of the majority of papers dealing with spectrographic methods of chemical analysis that were published during the period stated. Some earlier papers are also included.

The sections comprise the following: I, a list of some two hundred papers arranged under authors' names; II, substances analyzed, with an indication of the methods used and some of the results obtained; III, apparatus; IV, methods; V, general; VI, books. Complete cross references are given. It is intended as a guide to the scattered literature for those who seek further information on their own problems. This purpose is usefully fulfilled. An attempt is made to indicate the relative value of the various papers, but this makes one wish for a more extended critical survey.

M. MILBOURN.

Statistical Physics. By L. LANDAU AND E. LIFSHITZ. Translated from the Russian by D. Shoenberg. viii + 234 pp. New York: Oxford University Press, 1938. Price: \$6.00.

In this book the authors aim "to give a unified presentation of thermodynamics and classical statistics, based on the point of view associated with the name of Gibbs."

The first chapter introduces the concepts of probability, mean values, and statistical independence, while in the second chapter the entropy is defined statistically and the law of increasing entropy is formulated. The various thermodynamic functions are discussed in the third chapter, and the Gibbs distribution in the fourth. In the following chapter the thermodynamic functions are evaluated for a perfect gas, for a mixture of perfect gases, for an imperfect gas, and for a solid. Chapter VI is devoted to fluctuations and thermodynamic inequalities; it includes a discussion of the LeChatelier-Braun principle. Chapter VII introduces the chemical potential, and in chapter VIII phase equilibrium is studied. Chapter IX deals with solu-

tions and includes a fairly extensive discussion of equilibrium curves. After a brief discussion of chemical reactions in chapter X, there is presented in chapter XI a valuable treatment of anisotropic bodies. Transition points (including Curie points) and order and disorder in solids and in solid solutions are treated in a clear manner. The book concludes with a brief discussion of surface phenomena, including adsorption, the formation of nuclei, and the growth of crystals.

This book is highly recommended to students, who will find in it an excellent treatment of the equilibrium properties of matter based on classical statistics.

F. H. MACDOUGALL.

British Chemical Industry. By SIR GILBERT T. MORGAN AND DAVID DOIG PRATT. 372 pp. New York and Toronto: Longmans, Green and Company, 1938. Price: \$6.25.

This book is a collection of public lectures delivered at the University College of Wales. It is not a textbook, but it can be used as such. Its contents have been strictly limited to the British practice of chemical manufacture. The subject matter is arranged under the raw materials, the availability of which from both domestic and foreign sources accounts for particular practices. Both the inorganic and organic industries are included in the sixteen chapters.

Each chapter begins with statements as to the availability of the raw materials. Most of the individual subjects have an historical sketch of a process of development which is both interesting and valuable. Reasons for using certain methods and applying changes in methods are given. Chemical reactions, conditions of operations, statistics, and numerous illustrations of equipment are included.

Though many of the subjects are treated at some length with considerable detail, others are passed over hurriedly. This is true of the organic processes. Further application of physical chemistry and the unit chemical engineering operations would have made this book more satisfactory for teaching purposes, but presumably that was not the intention of the authors.

This is a very interesting, informative, and valuable book. It contains many good illustrations. It is well written and is very readable.

CHARLES A. MANN.

Combustion, Flames and Explosions of Gases. By BERNARD LEWIS AND GUENTHER VON ELBE. 415 pp. Cambridge: University Press, 1938. New York: The Macmillan Company, 1938. Price: \$5.50.

This monograph, which has been needed for a number of years, should be especially valuable to engineers interested in the more technical aspects of gaseous combustion and to students of the kinetics of gas reactions. To the former group it will serve as an introduction to the theoretical background of the subject and in addition will furnish a worthwhile correlation of the outstanding experimental results in terms of these theories. The latter group will find it valuable chiefly for its systematic and coördinated survey of the highly complex but interesting phenomena of flame propagation.

The four parts into which this book is divided are entitled, "Chemistry and Kinetics of the Reactions between Fuel Gases and Oxygen," "Propagation of Flames," "State of the Burnt Gas," and "Problems in Technical Combustion Processes." In addition, rather extensive tables of pertinent thermodynamic quantities, of limits of inflammability, and of flame temperatures are appended. The introductory chapter of the first section consists of a brief description of the theories of chain reactions, and is written largely from the viewpoint of Hinshelwood. In the two following chapters, the experimental results on the combustion of hydrogen and of

hydrocarbons are interpreted in terms of these theories. This is followed by discussions of the emission spectra of the flame front and of the ignition of combustible mixtures by sparks. The second part, which in the reviewer's opinion is the most interesting section of the book, is devoted to a discussion of the propagation of flames under stationary, expanding, and detonating conditions. What might be called the thermodynamic properties of flames and of the products of combustion are discussed in the third part of the book. This section is introduced by a brief outline of the methods of obtaining the values of the thermodynamic functions of simple gases from spectroscopic data. The fourth part, which is only twenty-eight pages long, consists largely of an account of combustion processes occurring in internal-combustion engines.

The book is excellently printed and is well illustrated by a number of line drawings and half-tone reproductions of photographs.

ROBERT LIVINGSTON.

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